Barriers impairing mineral bioaccessibility and bioavailability in plant-based foods and the perspectives for food processing

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Journal: Critical Reviews in Food Science and Nutrition

Submitted: May 2018

Resubmitted: November 2018

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Abstract

Plant-based foods gain more importance since they play a key role in sustainable, low-meat and healthy diets. In developing countries, these food products, especially legumes and cereals, are important staple foods. Nevertheless, the question arises on how efficient they are to deliver minerals and if it is useful to encourage their consumption to reduce the prevalence of mineral deficiencies? This review paper focuses on the discrepancy between the mineral content and the amount of minerals that can be released and absorbed from plant-based foods during human digestion which can be attributed to several inherent factors such as the presence of mineral antinutrients (phytic acid, polyphenols and dietary fiber) and physical barriers (surrounding macronutrients and cell wall). Further, this review paper summarizes the effects of different processing techniques (milling, soaking, dehulling, fermentation, germination and thermal processing) on mineral bioaccessibility and bioavailability of plant-based foods. The positive impact of these techniques mostly relies on the fact that antinutrients levels are reduced due to removal of fractions rich in antinutrients and/or due to their leaching into the processing liquid. Although processing can have a positive effect, it also can induce leaching out of minerals and a reduced mineral bioaccessibility and bioavailability.

Keywords: Minerals, dietary fiber, phytic acid, polyphenols, physical barriers, processing

1. Introduction

Plant-based foods, including vegetables, fruits, cereals and legumes, are important ingredients in the human diet all over the world (Global Dietary Database 2010). These food products are, for example, becoming increasingly important due to sustainability reasons. Especially in developing countries, plant-based foods represent a high proportion of the dietary intake

(Tontisirin, Nantel and Bhattacharjee 2002). To these populations, plant-based food systems provide not only macronutrients but are also the main source of micronutrients, such as minerals, which are defined as chemical elements required by organisms to perform vital functions (Berdanier, Dwyer and Heber 2013). Minerals are classified as essential nutrients as they cannot be synthesized by the human body, and must be obtained from the diet. This review paper focusses on iron and zinc because of their important physiological role in the human body and because iron and zinc deficiencies have been reported to be prevalent nutritional problems all over the globe (Platel and Srinivasan 2016). Iron participates in a wide variety of metabolic processes, including respiration, energy production, DNA synthesis, and cell proliferation, whereas zinc has been shown to be essential to the structure and function of a large number of macromolecules and for more than 300 enzymatic reactions (Tapiero and Tew 2003; Belitz, Grosch and Schieberle 2009; Hentze et al. 2010). The recommended nutrient intake for iron and zinc is on average respectively 13.7 and 14 mg per capita per day for adult males and 29.4 and 10 mg per capita per day for women of reproductive age (FAO and World Health Organization 2004).

When food is consumed, the present nutrients can be released from the matrix, followed by conversion into absorbable units which can subsequently be absorbed into the bloodstream and transported to their respective target tissues (Boland, Golding and Singh 2014). The nutrient fraction which is released from the food matrix and available for absorption is referred to as bioaccessible (which can be, for example, determined *in vitro*), whereas the nutrient fraction which is absorbed and available for utilization in physiologic functions and storage is referred to as bioavailable (examined by *in vivo* experiments or cell cultures) (Fernández-García, Carvajal-Lérida, and Pérez-Gálvez 2009). In contrast to macronutrients, biochemical conversion during digestion of micronutrients into absorbable units is not needed, since they

are absorbable as such, with or without a specific carrier (Basu and Donaldson 2003; Jackson and McLaughlin 2009).

Absorption of iron and zinc mainly takes place in the small intestine (Sitrin 2014). Although evidence has been found for colonic absorption of other minerals, such as calcium, there is little data to suggest a similar capacity for iron and zinc (Takeuchi et al. 2005, Gopalsamy et al. 2015). In the case of iron, an important distinction should be made between heme iron and non-heme iron. Heme iron, particularly present in animal-based foods, consists of iron complexed with the porphyrin ring from either haemoglobin or myoglobin (Pizarro et al. 2016). Absorption is mediated through heme iron specific receptors on the microvilli of enterocytes. Once absorbed, the iron is split from the complex by heme oxygenase (Fuqua, Vulpe and Anderson 2012). The second type of iron is non-heme iron from plant based-based foods. Within non-heme iron, a distinction must be made between iron in the ferrous state (Fe^{2+}) and the ferric state (Fe^{3+}). The divalent metal transporter 1 (DMT1) transports non-heme iron in the ferrous state together with protons across the mucosal membrane. The non-heme iron in the ferric state must be reduced before it can be absorbed using the same mechanism (Ganong 1995; Bohn, Meyer and Rasmussen 2008; Fuqua, Vulpe and Anderson 2012; Sitrin 2014). Zinc is absorbed in the small intestine by a carrier (ZnT-1) -mediated mechanism (Krebs 2000; Roohani et al. 2013).

Plant-based foods are expected to become more important in the human diet. As the global population is rising, the pressure will increase on animal-based foods and more sustainable food sources will be needed, e.g. legumes. However, an increase in consumption of plant-based foods could also have consequences for human health. Therefore, this review paper will focus on these plant-based food products. Even though plant-based foods are intrinsically rich in minerals such as iron and zinc (Table 1), it has been reported that their release from the food

matrix during digestion might be limited, thereby reducing the amount available for absorption (Platel and Srinivasan 2016).

Among others, the low bioaccessibility and bioavailability of non-heme iron and zinc from plant-based foods can be attributed to several inherent barriers for mineral digestion, of which antinutrients and physical barriers seem to be the most important (Rossander, Sandberg and Sandström 1992; Shahidi 1997; Mishra, Hardcare and Monro 2010; Platel and Srinivasan 2016). On the one hand, mineral antinutrients (e.g. dietary fibers, phytic acid and polyphenols) can bind the minerals, potentially inhibiting their release for absorption. The effect of these antinutrients on mineral bioaccessibility depends on the digestibility of the chelate (antinutrient-mineral complex) (Svarc-Gajic 2013; Baye, Guyot and Mouquet-Rivier 2017). Besides binding minerals in the plant-based food systems *in situ*, antinutrients, originating from other simultaneously ingested food ingredients, are also believed to form complexes with dietary minerals (Kumar et al. 2010). On the other hand, physical barriers (e.g. the cell wall and the digestibility of the surrounding food matrix) for digestion can be present in plant-based foods and thus impede both mineral bioaccessibility and bioavailability (Glahn et al. 2016).

As a consequence, even when dietary recommendations are met, mineral deficiencies can originate due to impaired mineral absorption. In fact, mineral undernutrition, especially iron and zinc deficiencies, are reported to be prevalent nutritional problems all over the globe (Platel and Srinivasan, 2016). According to the WHO report (2015), iron deficiency is the most common micronutrient deficiency in the world, affecting over 30% of the world's population, including a large number of children and women in developing countries. Moreover, iron deficiency is believed to be the only micronutrient deficiency that is also significantly prevalent in industrialized countries (World Health Organization 2015). In particular, many women suffer from iron deficiency during pregnancy due to increased iron demand for foetal growth

and development, a condition that is strongly linked to low birth weight, premature delivery, and a multitude of perinatal complications. Alongside being a major factor contributing to the development of anaemia, iron deficiency can cause disturbances in the functioning of both the endocrine and immune systems (Bailey, West and Black 2015). Next to iron, zinc deficiency is also a worldwide health problem with about 33% of the world's population at risk, particularly those in underdeveloped countries. Low zinc blood levels may lead to numerous clinical symptoms, including growth retardation, impaired brain development and cognitive performance, poor wound healing, diarrhoea, infertility and increased risk of infections (Wapnir 2000; Crook 2011).

Next to insufficient dietary intake and physiological status of consumers (e.g. malabsorption and illness), the poor bioaccessibility and bioavailability of minerals from plant-based foods could potentially contribute to the high prevalence of mineral deficiencies (Manary et al. 2000). This review paper focuses on the influence of particular mineral antinutrients (*cfr.* §2) and the physical barriers (*cfr.* §3) on the bioaccessibility and bioavailability of iron and zinc in plant-based foods. In addition, the perspectives of different processing techniques to modify the bioaccessibility and bioavailability of iron and zinc in plant-based foods are discussed (*cfr.* §4).

2. Antinutrients influencing mineral bioaccessibility and bioavailability

“Antinutrients are natural or synthetic compounds that interfere with the absorption of nutrients” (Oxford Dictionary of Biochemistry and Molecular Biology 2006), in this way they reduce the nutrient bioaccessibility and bioavailability from food. Antinutrients are abundantly present in plant-based foods since they play a physiological role in the chemical defence mechanisms against various insects, pests and humans of the plant (part) where they originate from (Svarc-Gajic 2013). Many *in vitro* (Persson et al. 1991; Olivares et al. 2001; Glahn et al. 2002; Bosscher et al. 2003; Lestienne et al. 2005; Andrews et al. 2014; Suliburska and Krejpcio

2014) and *in vivo* (Drews, Kies and Fox 1979; Larsson et al. 1996; Hurrell et al. 2003; Schlegel, Nys, and Jondreville 2010; Luo and Xie 2012; Miyada, Nakajima and Ebihara 2012) studies have reported the negative consequences of dietary fibers (*cfr.* §2.1) phytic acid (*cfr.* §2.2), polyphenols (*cfr.* §2.3) and on iron or zinc bioavailability. Since these compounds specifically can interfere with the absorption of minerals, they are generally referred to as mineral antinutrients. Although it seems interesting trying to reduce the mineral antinutrient concentration in plant-based foods in order to increase mineral bioaccessibility and bioavailability, it should not be forgotten that these compounds can possess other health-promoting effects as well (*cfr.* *infra*).

2.1 Dietary fiber

Dietary fiber was traditionally defined as the non-digestible components of the plant cell wall (Hipsley 1953). Most recently, dietary fiber is described as “edible carbohydrate monomers (naturally occurring in foods, as well as isolated, modified and synthetic polymers with proven physiologic effects of benefit to health) with ten or more monomeric units, which are not hydrolysed by the endogenous enzymes in the small intestine of human” (Joint FAO/WHO Food Standards Programme Commission 2016). Dietary fibers can be classified into water soluble and water insoluble fibers based on their solubility in water at a defined pH. Water soluble fibers (e.g. pectin, inulin and polydextrose) are fermented in the colon while water insoluble fibers (e.g. cellulose, hemicellulose, lignin and resistant starch) have bulking effects but may only be fermented to a limited extent in the colon. Fruit and vegetables have a significantly higher proportion of soluble dietary fiber while cereals and legumes contain more insoluble dietary fibers (Figuerola et al. 2005; de Almeida Costa et al. 2006). Several components of dietary fiber, such as the free carboxyl group on some sugar residues, uronic acid and the surface hydroxyl group of cellulose are reported to possess the ability to bind minerals (Schneeman 1986). Moreover, dietary fiber may be associated with many other

substances, mostly with proteins, polyphenols and phytic acid, which are believed to also affect its mineral binding capacity (Idouraine et al. 1995; Vitali et al. 2008). Various *in vitro* studies have shown that the binding of minerals might be affected by the source of fiber, pH and other physicochemical properties of dietary fiber (Thompson and Weber 1979; Camire and Clydesdale 1981; Garcia-Lopez and Lee 1985; Platt and Clydesdale 1987; Persson et al. 1987).

Since several dietary fiber components have the ability to bind minerals, these minerals become embedded in an insoluble and/or unabsorbable fiber-mineral complex which cannot be hydrolysed by human digestive enzymes. These minerals can only be released if fermentation of the fiber takes place in the colon, but mineral absorption has generally been accepted to occur mainly in the small intestine (Torre, Rodriguez and Saura-Calixto 1995). Consequently, the extent to which fermentation (breakdown of the fiber-mineral complex) in the colon contributes to mineral bioaccessibility and bioavailability is still a point of discussion. Moreover, for some complexes, limited fermentation is hypothesized. Because of this complex formation, by either electrostatic forces or chelation, or due to the anion exchange capacity, dietary fiber can be considered as a mineral antinutrient. The influence on mineral bioaccessibility and bioavailability of fibers depends on specific characteristics of the fiber. For example, the solubility of the fiber plays an important role.

Soluble dietary fiber

Among the soluble dietary fibers, pectin is abundantly present in the cell wall of plant-based food systems such as fruits, vegetables and legumes (Chan et al. 2017). Pectin is a heteropolysaccharide, predominantly containing galacturonic acid (GalA) residues, in which varying proportions of the acid groups are present as methoxyl esters, while a certain amount of neutral sugars might be present as side chains (Voragen et al. 2009). The non-methylesterified GalA residues can be ionised (depending on the pH of the system) giving pectin its polyanionic nature

and ability to bind metal-ions. The interaction between pectin and divalent cations is known to generally occur according to the egg-box model (Caffall and Mohnen 2009) and is represented in Figure 1. Changes in the degree of methylesterification (DM) of pectin will influence its polyanionic nature and the mineral binding capacity. In addition, the presence of neutral sugars as well as the degree and nature of branching are reported to influence the cation binding capacity of pectin (Kyomugasho et al. 2017). Besides a reduced degree of esterification, Celus et al. (2018) showed that the pattern of DM (blockwise or randomly), was shown to affect Zn^{2+} or Ca^{2+} binding capacity of pectin: the more blockwise its pattern of DM, the higher its mineral binding capacity. A schematic representation of structural characteristics of pectin which can influence pectin-mineral binding capacity is shown in Figure 2. Reduced mineral bioavailability, caused by the presence of pectin, has been reported. Bosscher et al. (2003) used an *in vitro* dialysis model to evaluate the availabilities of calcium, iron, and zinc from infant formulas supplemented with soluble dietary fiber fractions. They found that pectin reduces iron bioaccessibility, which correspond with the *in vitro* data of Platt and Clydesdale (1987) as well as with the *in vivo* data of Monnier, Colette and Mirouze (1980). In addition, *in vitro* studies by Kyomugasho et al. (2015) and Celus et al. (2018), reported that the bioaccessibility of calcium-, zinc- and/or iron-ions decreases with increasing electrostatic pectin-interactions (i.e. lower degree of esterification).

As mentioned before, the mineral binding capacity of fiber can be influenced by the association of the fiber with other substances. In this context, Persson et al. (1987) investigated the mineral binding capacity of soluble fiber fractions of wheat bran and whole grain wheat bread dough, in which most of the phytic acid was present. They found these fractions interacting strongly with the metal ions, but incubation of these fractions with phytase reduced the complexing ability, indicating the active ligand was phytic acid.

Insoluble dietary fiber

In contrast to soluble dietary fibers, which can interact strongly with metal ions, the mineral binding capacity of insoluble dietary fibers is negligible (Persson et al. 1987). Among insoluble fibers, lignin was shown to have more mineral binding capacity than cellulose and hemicelluloses, probably because of its polyphenolic nature (Fernandez and Phillips 1982).

The negative influence of dietary fibers on mineral bioavailability is not only due to their ability to bind minerals, but the presence of dietary fibers in the diet can induce a higher digest viscosity which can impede the contact between nutrients and digestive enzymes, and consequently limit the availability of nutrients for absorption (Guillon and Champ 2000).

Positive health effects of dietary fiber

Although there is evidence that high fiber intake can hinder mineral absorption, the subject is controversial (Idouraine et al. 1995). For instance, in the previously mentioned study, Bosscher et al. (2003) have shown soluble dietary fiber to affect mineral bioavailability not only in a negative way, but also positively, depending on the type of dietary fiber. The fermentation of fibers, such as inulin and fructooligosaccharides (most common dietary source is wheat), in the colon can also enhance mineral absorption. During their fermentation by colonic microbiota, short chain fatty acids are produced. These components can trigger increased proliferation of epithelial cells, which, in turn, increase the absorptive surface area and hence absorption of nutrients (Roberfroid 2007; Baye, Guyot and Mouquet-Rivier 2017). Additionally, short chain fatty acids can decrease luminal pH and thus create an acidic environment, which is more favourable for mineral solubility (Wang et al. 2010). The positive effect of the presence of inulin and fructooligosaccharides on mineral absorption has been shown in several animal studies (Delzenne et al. 1995; Ohta et al. 1995; Younes, Demigné, and Rémésy 1996; Charles Coudray et al. 2003; Lobo et al. 2009) and is partially confirmed in humans (Coudray et al. 1997; Ellegard, Andersson and Bosaeus 1997; Van Den Heuvel et al. 1999; Tahiri et al. 2003;

Ducros et al. 2005; Yap et al. 2005) as reviewed by Coudray et al. (2003). The absorption enhancing properties of fibers depends on specific characteristics of the fiber. Improved mineral absorption has been shown for some soluble dietary fibers such as inulin, fructooligosaccharides and pectin while this effect was not observed for insoluble ones (Greger 1999; Sakai et al. 2000). In another *in vivo* study, Kim et al. (1996) demonstrated that pectin structural properties, including both molecular weight and degree of esterification, can influence the mineral binding properties of pectin. They showed that low molecular weight pectins with a high degree of esterification were able to improve the absorption of minerals. However, in high molecular weight pectins with a low degree of esterification these effects were absent.

2.2 Phytic acid

Phytic acid (Figure 3), known as myo-inositol hexaphosphate (IP6) or phytate when in the salt form, serves as the major phosphorus storage form in many plant tissues. According to Oatway, Vasanthan and Helm (2001) and Sandberg (2002), phytic acid is most abundant in plant-based foods such as cereal grains, legumes, nuts and oilseeds comprising 1-5% and it can appear in lower amounts in roots, tubers and vegetables (Gupta, Gangoliya and Singh 2015). Phytic acid is formed during the maturation stage of the plant seed and contains 60-90% of the total phosphorus content in dormant seeds, where it is accumulated as mixed salts of several cations, including iron, zinc, magnesium, calcium and potassium (Frossard et al. 2000; Kumar et al. 2010). Due to the presence of phytase, phytic acid can be hydrolyzed into lower inositol-phosphates (e.g. inositol penta- (IP5), tetra- (IP4) or triphosphate (IP3)).

In this context, phytic acid is a well-known mineral antinutrient that has been intensively investigated throughout the years as reviewed by Harland and Morris (1995), Oatway, Vasanthan and Helm (2001), Schlemmer et al. (2009) and Kumar et al. (2010). This mineral antinutrient exists as a strongly negatively charged ion over a wide pH range (from pH > 2.0)

and it is able to form stable complexes with divalent or trivalent mineral ions such as iron, zinc, calcium and magnesium through electrostatic interactions (Kumar et al. 2010). The complex between phytic acid and minerals can occur either in the plant tissue and/or in the digestive tract. Minerals bind to phytic acid with a strength proportional to their atomic mass and electronegativity. Therefore, zinc and copper have been found to form stronger complexes with phytic acid than lighter atoms, such as iron and calcium (Vohra, Gray and Kratzer 1965; Oberleas and Chan 1997). These complexes, phytates, are not easily digestible by monogastric animals, such as humans, due to the lack of endogenous phytase enzymes (Hurrell and Egli 2010). As such, the bioavailability of the bound ions is impaired. According to Sandberg, Carlsson and Svanberg (1989) and Sandström and Sandberg (1992), mainly higher inositol-phosphates (e.g. IP6 and IP5) have a negative effect on mineral bioavailability, given that lower inositol-phosphates (e.g. IP4 and IP3) have a lower capacity to bind minerals and generally form more soluble complexes.

In other words, among the essential minerals, zinc has the highest binding strength for phytic acid and as a result thereof, zinc absorption is hypothesized to be more negatively influenced by phytic acid than iron absorption. At marginal dietary zinc supply, the inhibitory effects of phytic acid on zinc bioavailability can be predicted by the molar ratio of phytic acid to zinc in the diet. Davis and Olpin (1979) found that molar ratios exceeding 10:1 (phytic acid:zinc) have a negative influence on zinc absorption. More recently, Ma (2007) reported that when at a molar ratio of 16:1, zinc is no longer bioavailable. The inhibitory effect of phytic acid on zinc bioavailability has been reproduced and confirmed in several studies (Lestienne et al. 2005; Viadel, Barberá and Farré 2006; Schlegel, Nys and Jondreville 2010; Kruger et al. 2013). In addition, high levels of calcium strengthen the inhibitory effect of phytic acid on zinc absorption since zinc coprecipitates with phytic acid and calcium as a zinc-calcium-phytate complex. This complex is even less soluble than phytate complexes formed with either one ion

alone (Lopez and Leenhardt 2002). Since most plant-based foods possess a high calcium amount compared to zinc, this can be of major concern. For example, depending on the legume type, calcium:zinc ratios up to approximately 25:1 have been reported by Eskin and Shahidi (2013). Additionally, gastrointestinal secretions may contain ions as well (Boland, Golding and Singh 2014), which can bind phytic acid in the gastrointestinal tract during digestion.

Phytic acid is also capable of complexing with iron in the same way as previously described for zinc. This iron-(calcium-)phytate complex precipitates, withdrawing the iron from the digest and renders it unavailable for absorption. In an *in vitro* study by Lestienne et al. (2005), it was observed that both iron and zinc bioaccessibility of whole pearl millet flour were significantly improved by phytic acid degradation and removal. However, since dephytinization of the bran fraction had no effect on either iron or zinc bioaccessibility, they concluded that even if phytates are involved in reducing iron and zinc bioaccessibility in pearl millet flour, fibers and tannins may also play an important role by chelating a high proportion of iron and zinc in grain hulls. Next to *in vitro* studies, *in vivo* studies reported the negative effect of phytic acid on iron absorption. The negative effect of phytic acid on iron absorption has, for instance, been shown by performing a cell culture study using model systems (Andrews et al. 2014). Caco-2 cells were incubated with iron for 24 h and subsequently challenged with phytic acid, pectin or tannic acid for another 24 h. Finally, iron uptake was determined. The results were as expected: phytic acid, pectin or tannic acid each decreased the iron uptake and addition of calcium to phytic acid strengthened its inhibitory effect. Hallberg, Brune and Rossander (1989) showed the inhibitory effect of sodium phytate on iron absorption in man by serving wheat rolls containing no phytates and rolls to which various amounts were added just before serving. In this study, the negative effect of phytic acid has also been shown to be dose dependent. They showed that 10 mg/100 g, 20 mg/100 g and 100 mg/100 g phytic acid reduced iron absorption by 20%, 40% and 60%, respectively. These results were confirmed by Petry et

al. (2010) who served dephytinized and nondephytinized red bean porridge to young women. In addition, Saha, Weaver and Mason (1994) showed that iron absorption in rats decreased significantly when the molar ratios of phytic acid to iron were above 14:1. For example, 100 g beans (*phaseolus vulgaris*) can contain up to 2.38 g phytic acid and up to 14 mg iron (dry weight), this means that in realistic cases the ratio exceeds 14:1 (Schlemmer et al. 2009; Hayat et al. 2014).

Besides its role in mineral bioavailability, phytic acid can also influence protein digestibility. This complex formation with proteins alters the protein structure, which make the proteins less soluble, and affects the enzymatic degradation and peptic digestion (Kumar et al. 2010).

Positive health effects of phytic acid

Although the presence of phytic acid in the human diet can have a negative impact on mineral bioavailability and protein digestibility, phytic acid has been shown to be protective to a variety of cancers (Jenab and Thompson 2001). It has been suggested that phytic acid is a potent inhibitor of the iron-mediated generation of the hazardous oxidant, hydroxyl radical (as described in section 2.3). Graf and Eaton (1985) have proposed that inhibition of intracolonic hydroxyl radical generation, for example via the chelation of iron ions by phytic acid, may help to explain the suppression of colonic carcinogenesis and other inflammatory bowel diseases by diets rich in phytic acid.

2.3 Polyphenols

Polyphenols are an integral part of the human diet since they are omnipresent in plant tissues, where they serve as protective substances against harmful external influences (e.g. ultraviolet radiation and aggression by pathogens) (Pandey and Rizvi 2009). Phenolic compounds are composed of an aromatic ring with at least one hydroxyl group in their structure. In plants, the majority of polyphenols are conjugated to one or two sugar moieties. Other compositions, for

instance with amines, lipids and organic or carboxylic acids make up the remaining part (Bravo 1998). Polyphenolic compounds can be classified based on the number of phenol rings and their linkages. In plants, the majority of polyphenolics are represented by flavonoids (low molecular weight phenolic compounds, including anthocyanins) and tannins (intermediate to high molecular weight phenolic compounds, also referred to as polymeric flavonoids). The common structure of flavonoids is a diphenylpropane ($C_6-C_3-C_6$) and consists of two aromatic rings linked through three carbons that usually form an oxygenated heterocycle (Figure 4). The best known tannin is tannic acid that consists of a hepta- to octa-galloyl- β -D-glucose in which, on average, two to three additional galloyl groups are esterified to a preexisting β -1,2,3,4,6-pentagalloyl-D-glucose core (Figure 5) (Haslam 1992; Liu et al. 2005). The occurrence and amount of polyphenols may vary from plant to plant (mainly depending on genetic factors and environmental conditions), however, they are generally concentrated in the seed coat of plant-based food products. Tea (75-105 mg/100 ml), coffee (130-350 mg/100 ml), fruit juices (0.2-710 mg/100 ml) and red wine (100-650 mg/100 ml) are the most abundant dietary sources, while vegetables (e.g. leek: 20-40 mg/100 g dm), cereals (e.g. wheat: 22-40 mg/100 g dm) and legumes (e.g. chickpeas: 78-230 mg/100 g dm) also contribute to the total polyphenol intake (Bravo 1998; Belitz, Grosch and Schieberle 2009; Quideau et al. 2011).

Depending on the type of flavonoid structure, polyphenols can exhibit metal chelating properties. If polyphenols and metal cations are present together in the food matrix and/or the digestive tract, the metal cations can interact with hydroxyphenyl and carboxyl groups of the polyphenols. A general iron-polyphenol complex is illustrated in Figure 6. Intestinal absorption of these complexes is influenced by their molecular weight, degree of glycosylation and esterification. In the case these complexes are absorbed, most polyphenols are quickly eliminated in urine and bile without release of the bound minerals during the polyphenol

metabolism (Scalbert et al. 2002). In other words, polyphenolic compounds can reduce mineral bioaccessibility and bioavailability and are therefore considered as antinutrients (Bravo 1998).

The mineral chelating capacity of polyphenols has mainly been explored in relation to iron. Several *in vitro* studies have reported the high iron chelating capacity of both flavonoids (Mira et al. 2002; Ryan and Hynes 2007; Mladěnka et al. 2011) and tannins (Yoneda and Nakatsubo 1998; Iffat, Maqsood and Fatima 2005; Karamać 2009). Due to this iron chelating capacity (principally taking place in the gastrointestinal lumen during human digestion), flavonoids and tannins have been associated with a reduced absorption of iron from the human diet (Disler et al. 1975; Brune, Rossander and Hallberg 1989; Hurrell, Reddy and Cook 1999; Layrisse et al. 2000; Petry et al. 2010).

Zinc, as compared to iron, has a lower affinity for polyphenols, particularly at neutral and acidic pH (Santos-Buelga and Scalbert 2000). Only few *in vivo* studies examined the effect of polyphenol-rich foods (e.g. tea and red wine) on zinc absorption. For example, Ganji and Kies (1994), showed that tea consumption has a small but not statistically significant adverse effect on zinc bioavailability in humans. However, Coudray et al. (1998) reported that phenolic compounds may decrease intestinal absorption of zinc in rats. In a subsequent study, Coudray et al. (2000) showed that the short- or long-term consumption of red wine did not have a negative effect on intestinal absorption or tissue levels of zinc in rats. The absence of an effect of red wine on zinc absorption may be due to the antagonist actions of polyphenols and ethanol. More research should be performed to investigate the effect of polyphenol-rich foods on zinc absorption.

Beyond their mineral binding capacity, polyphenols can form insoluble complexes with dietary proteins, starch and other carbohydrates, reducing the digestibility of these nutrients. In

particular, the presence of tannins in food has been considered as an antinutritional aspect due to their well-known capacity to bind and precipitate proteins (Svarc-Gajic et al. 2013).

Positive health effects of polyphenols

Although the metal chelating activity of polyphenols can have a negative impact on mineral bioavailability, this action can be beneficial in certain circumstances. Iron can be the initiator of hydroxyl radical production by the Fenton and Haber-Weiss reactions (Figure 7).

By chelating this mineral, the production of reactive oxygen species (ROS) can be prevented, consequently chelation of iron is one of the ways polyphenols exert their antioxidant capacity (Bravo, 1998). Additionally, polyphenolic antioxidants (PPH) can interfere with the oxidation of lipids and other molecules by rapid donation of a hydrogen atom to radicals (ROO• and RO•):

The formed phenoxy radical intermediates (PP•) are relatively stable and therefore a new chain reaction is not easily initiated. The phenoxy radical intermediates also act as terminators of the propagation route by reacting with other free radicals:

Concludingly, by preventing the formation of ROS and/or scavenging ROS, polyphenols can slow down lipid oxidation and non-enzymatic browning during food storage on the one hand, and on the other hand oxidative stress-related chronic diseases and age-related disorders such as cardiovascular diseases (e.g. atherosclerosis), carcinogenesis, neurodegeneration (e.g.

Alzheimer's disease), as well as skin deterioration can be prevented or reduced if polyphenols are consumed. Polyphenols are proven to be the most abundant antioxidants in the human diet (Brune, Rossander and Hallberg 1989; Bravo 1998; Mira et al. 2002; Mennen et al. 2005; Svarc-Gajic et al. 2013).

Although the antioxidant capacity of polyphenols is their most discussed characteristic, it should also be mentioned that polyphenolic compounds have been proven to be beneficial for human health through other mechanisms. For instance, because of their particular structural and conformational characteristics, polyphenols interact with specific biological targets (e.g. enzymes, transcription factors and receptors) (Fraga et al. 2010).

3. Physical barriers influencing mineral bioaccessibility and bioavailability

3.1 Cell wall

In the above sections of this paper, we have been discussing factors at the sub-cellular and molecular level that may affect mineral bioaccessibility and bioavailability. At the (multi-) cellular level, the plant cell wall has to be taken into account since many sources of food nutrients are swallowed in the form of intact plant tissue fragments (Boland, Golding and Singh 2014). Tissues of plant-based food systems are made up of cells which are surrounded by a cell wall. This cell wall provides the cell both structural support and protection. Within the plant cell, the cell wall structure is continuously modified, depending on the developmental stage and the environmental conditions. The plant cell wall can consist of three structural entities, namely the middle lamella, the primary cell wall and the secondary cell wall, but in plant-based food systems (fruits, vegetables, cereals and legumes) there rarely is a secondary cell wall present. The middle lamella in fruits, vegetables and legumes is rich in pectin and cements the cell walls of two neighbouring plant cells together. The primary cell wall is located next to the

middle lamella and mainly consists of pectin, cellulose and hemicellulose (Cafall and Mohnen 2009; Burton, Gidley and Fincher 2010; Burton and Fincher 2014).

The plant tissue structure has been known to influence the bioaccessibility and bioavailability of carbohydrates and other macronutrients as the cell wall may act as (partial) barrier to both digestive enzyme penetration into, and nutrient diffusion out of the fragment or particle (Mishra, Hardcare and Monro 2010; Pallares et al., 2019). Consequently, it can be questioned if the cell wall can be considered as a physical barrier for mineral bioaccessibility and bioavailability as well. During mechanical disruption of intact plant tissues (for example by chewing), the tissue may disintegrate by two possible tissue failure characteristics: cell breakage and/or cell separation (Figure 8) (Van Buggenhout et al., 2009). Depending on the composition and characteristics of the cell wall polymers, one of the tissue failure characteristics will be more prevalent. In the case of cell breakage, cell content is released and believed to be physically more available for digestive enzyme action or absorption in the digestive tract. However, if cell walls are not disrupted and the cell wall stays intact, nutrient/metabolite release kinetics might be influenced and nutrient availability might be reduced as such. Only recently this hypothesis for minerals has been investigated by Glahn et al. (2016), more specifically for iron in common beans. The cell wall of legumes, particularly of beans, has been shown to be microstructurally resistant to cooking and the digestion conditions and enzymes of the human intestinal tract. Therefore, Glahn et al. (2016) used relatively high intracellular pressure (>4000 psi) to initiate cell wall rupture but, surprisingly, this cell lysis did not result in a consistent or strong enhancement of bioavailable iron. They suggest that the liberated intracellular starch and protein influenced the iron bioavailability by creating a matrix that inhibited the exchange of iron with the cell transport mechanism. However, it should be noted that these results can also indicate that minerals which are bound

to cell wall material, are not being released due to cell lysis. These observations should be further investigated and for example confirmed by *in vivo* experiments.

3.2 Digestibility of the surrounding macronutrients

If macronutrients form a food matrix in which minerals are embedded remain undigested, it is hypothesized that they can form a physical barrier for mineral transfer to the absorption site in the small intestine (Glahn et al. 2016). Research has to be done to further examine this hypothesis.

4. Perspectives of food processing to impact mineral bioaccessibility

Food processing can increase food safety and stability, it can create desired process-induced flavours and can result in palatability improvement. Although there are many benefits, processing can also be detrimental, for example, by causing undesirable changes such as loss of colour, flavour, texture and smell (Considine et al. 2008). In addition, processing can affect the nutritional quality of foods. The nutritional quality of minerals in foods depends on their quantity as well as their bioaccessibility and bioavailability (Reddy and Love 1999).

In contrast to vitamins, minerals cannot be destroyed by light, heat, humidity, oxidizing or reducing agents and acids or bases (Miller 1996; Singh et al. 2007). However, on the one hand, food processing can affect the mineral content. Minerals can either be removed from foods during processing (leaching, physical separation) or processing can be responsible for mineral enrichment by addition or by transfer of minerals from other ingredients, machinery or packing material (Alegria et al. 2015). On the other hand, food processing can have an impact on mineral release from the food matrix.

The mineral concentration and the bioaccessibility and bioavailability of minerals from plant-based foods can, for example, be affected by milling (*cfr.* §4.1), soaking (*cfr.* §4.2), dehulling

(*cfr.*§4.3), fermentation (*cfr.*§4.4), germination (*cfr.*§4.5) and thermal processing (*cfr.*§4.6). These processes particularly affect the mineral concentration and by altering, degrading or removing antinutrients, the mineral bioaccessibility and bioavailability can be altered. In addition, several of these techniques are also believed to influence physical barriers.

4.1 Milling

Milling, a processing method commonly applied on raw cereal grains, has the objective to crush the grain into flour, whether or not combined with a (complete) separation of bran and germ from the endosperm (Belderok, Mesdag and Donner 2000).

Milling leads into tissue disruption whereby cell structures can be opened as well. On the one hand, this can enable the different components (e.g. minerals, antinutrients and enzymes) to come in more close contact, affecting mineral bioaccessibility and bioavailability (Raes et al., 2014). On the other hand, by disrupting the cell wall, it has been hypothesised this physical barrier for mineral bioaccessibility and bioavailability can be eliminated (Glahn et al. 2016). Cell wall breakage during mechanical disintegration can depend on previous processing steps. For example, mechanical disintegration of pulse seeds after cooking, may lead rather to cell separation than cell disruption, due to pectin solubilisation in the middle lamella (Dhital et al. 2016; Pallares et al. 2018). The intactness of cell wall structures, after cell separation, has been hypothesized to be a barrier for mineral bioaccessibility and bioavailability as discussed before (*cfr.*§3.1).

The effect of separation of bran and germ from the endosperm in cereal grains during milling can also influence the mineral concentration and mineral bioaccessibility and bioavailability. Cereal grains generally contain high levels of minerals in the bran and germ fractions (Ozturk et al. 2006; Eagling et al. 2014). By removing these fractions, endosperm with low mineral content leaves behind. For example, conversion of whole wheat to white flour can result in up

to 86% loss of iron, zinc, copper, magnesium and selenium (Miller 1996; Fardet 2010). However, not only minerals are removed since antinutrients like phytic acid, dietary fiber and tannins, are mainly found in the bran and germ fraction (Rendleman 1982; Dykes and Rooney 2007; Suma and Urooj 2014). For example, when milling is used to remove the bran and/or germ from cereal, up to 90% of the phytic acid content can be discarded (Gibson et al. 2010). Due to partial separation of the bran fraction of pearl millet, semi refined flour was low in antinutrients which improved the mineral bioaccessibility (Suma and Urooj 2014). Milling of cereals grains and separation of bran and germ from the endosperm in cereal grains during milling has been shown to enhance mineral bioaccessibility and bioavailability, although the content of minerals of milled cereals can be simultaneously reduced (Gibson et al. 2006; Oghbaei and Prakash 2013).

4.2 Soaking

Soaking of pulses and cereal grains is a widely applied technique at both household and industrial scales to soften their texture, to reduce the cooking time as well as to influence their nutritional value (Xu and Chang 2008). The technique consists of hydration of the seeds and grains in a soaking medium (mostly water), usually until they reach maximum weight. The nutritional value of these food products, in the context of mineral concentration and mineral bioaccessibility and bioavailability, is influenced by soaking in following ways: removal of antinutrients and minerals (leaking into the soaking medium), pH changes and hydrolysis of phytic acid (by activation of endogenous phytases). First, soaking has the potential to remove some antinutrients, which can be eliminated with the discarded soaking medium. However, the amount of removed antinutrients depends on the antinutrient type, pH and length and conditions of soaking (Gibson et al. 2006). Although it has been observed that soaking has the advantage of decreasing phytic acid and polyphenol levels of for example brown rice (Liang et al. 2008; Albarracín et al. 2013), sorghum (Mahgoub and Elhag 1998) and pulses

(Vijayakumari et al. 1998; Lestienne et al. 2005; Xu and Chang 2008; Khandelwal, Udipi and Ghugre 2010), simultaneously, it can also cause undesirable losses of minerals such as iron and zinc. Reduced levels up to 60 and 30% for iron and zinc respectively are reported after soaking for sorghum and pearl millet (Lestienne et al. 2005; Afify et al. 2011; Albarracín et al. 2013). It is therefore important to balance both positive and negative aspects of soaking treatments (Liang et al. 2008). Additionally, during soaking, pH changes may occur as well (Raes et al. 2014). Lowering the pH may reduce the complexation of bivalent minerals to pectin (Debon and Tester 2001; Kyomugasho et al. 2017), and in this way the amount of free iron and zinc can be increased. Further, due to the activation of phytase during soaking, phytic acid can be hydrolyzed into lower inositol-phosphates (e.g. IP4 and IP3), which have a lower capacity to bind minerals (Sandström and Sandberg 1992). It was reported that soaking cereals such as pearl millet with endogenous or exogenous phytase enzymes, at optimum conditions, significantly improved the *in vitro* bioaccessibility of iron and zinc by 2–23% (Lestienne et al. 2005). Additionally, Hurrell et al. (1992), showed that iron absorption from soy-protein isolates in humans increased four- to fivefold after an exogenous phytase treatment of the isolates.

4.3 Dehulling

When considering processing of pulses, dehulling, next to soaking, is commonly seen as one of the most applied processing techniques (Wang 2005). Pulse seeds are commonly composed of cotyledons and a seed coat. Upon dehulling, the seed coat of soaked pulses is removed and, in most cases, discarded (Black, Singh and Meares 1998). By discarding this fraction, both minerals and antinutrients can be removed. For example, it has been observed that the seed coat of different common bean varieties in general can contain over 85% of total calcium while cotyledons can contain over 75% of total potassium (Moraghan and Grafton 2002; Ribeiro et al. 2012). However, for minerals such as iron, zinc and copper, the accumulation can vary widely between seed coat and cotyledon fraction depending on the common bean variety

(Ribeiro et al. 2012). Concerning antinutrients, discarding the seed coat in pulse seeds does not necessarily lead to a decrease in phytic acid content, since it is mainly present in the cotyledons (Gibson et al. 2010). Contrarily, dietary fibers and tannins are primarily located in the seed coat and therefore their concentration in pulse seeds will decrease by removal of this fraction (Troszynska et al. 1997; Diaz, Caldas and Blair 2010; Shahidi et al. 2001; Sreerama et al. 2010; Eashwarage et al. 2017). Moreover, pectin in the seed coat of common beans has been shown to have structural characteristics important for binding minerals (*cfr.* §2.1) (Chigwedere et al. 2018). Because this physical separation technique is often combined with other processing methods, information on the effect of dehulling of pulses on the improvement of their mineral bioavailability is scarce (Ghavidel and Prakash 2007). In addition, the interplay between the removal of both minerals and antinutrients (e.g. dietary fibers and tannin but in many cases not of phytic acid) gives extra complexity to this manner. In this context, Luo, Xie and Cui (2010) reported that although faba beans were dehulled, they did not show significant increased iron and zinc bioavailabilities indicating that the reduction of the mineral content, by removing the seed coat, is an important factor.

4.4 Fermentation

Fermentation, initially applied as a preservation technique, depends on the biological activity of microorganisms for production of a range of metabolites which can suppress the growth and survival of undesirable microflora in food products (Ross, Morgan and Hill 2002). Nowadays, fermented foods are consumed both in developing and industrialised countries, not only for the benefit of preservation and safety, but also for their sensory characteristics (e.g. flavour, aroma and texture) (Holzapfel 2002). During non-spontaneous fermentation, raw, soaked and/or heated pulse seeds or cereal grains, in a moist solid state, are inoculated with (various) microorganisms (Holzapfel 2002). There are three main kinds of microorganisms used in the fermentation of pulses and cereals: lactic acid bacteria, bacteria of the genus *Bacillus*,

Aspergillus fungi and yeasts (Raes et al. 2014). Some microorganisms associated with fermented foods, are capable of producing enzymes (e.g. phytase and polyphenol oxidase) which can degrade antinutrients such as phytic acid and polyphenols. Additionally, lactic fermentation leads to lowering of pH as a consequence of production of organic acids, mainly lactic acid, which is favourable for endogenous phytase and polyphenol oxidase activity (optimal pH ranges from 4.5 to 6.0) (Konietzny and Greiner 2002; Sandberg 2002; Towo, Matuschek and Svanberg 2006). Moreover, a pH change can affect the complexation of antinutrients with minerals, as mentioned in §4.2, and an acidic environment may result in abstraction of hydride ions and rearrangement of phenolic structures (Towo, Matuschek and Svanberg 2006). Incorporation of these organisms into starter cultures may, therefore, improve mineral bioaccessibility and bioavailability (Gibson and Hotz 2001; Duhan, Khetrapaul and Bishnoi 2004). Besides degrading phytic acid and polyphenol content, fermentation could also improve mineral bioavailability by virtue of the formation of organic acids, which can form soluble and absorbable ligands with the minerals, thereby preventing the formation of insoluble complexes with for example phytic acid (Sandberg 2002; Hemalatha, Platel and Srinivasan 2007; Sokrab, Ahmed and Babiker 2014).

4.5 Germination

This process, whereby dry pulses and cereal grains are soaked in water, drained of water and allowed to germinate in humid and warm (20-30°C) environments, results in the start of a sequence of biochemical reactions. For example, germination leads to an increase in phytase activity through *de novo* synthesis and/or activation of endogenous phytase. Phytase activity during germination is needed to mobilize phosphorus from phytic acid, as it is required for the growth of the new seed. Relative to the soaking process, an increase in phytate degradation of 4-50% is observed in sorghum and millet, depending on the type of pulse or cereal grain studied (Eyzaguirre et al. 2006; Afify et al. 2011). In addition, Hemalatha, Platel and Srinivasan (2007)

and Kayodé et al. (2013) observed a decrease in tannin content in several pulses and cereal grains after germination. The loss of phenolic compounds during germination could be due to enzymatic activity (polyphenol oxidase), conversion into other phenolics, leaching, and complex formation with proteins. Hemalatha, Platel and Srinivasan (2007) reported that germination of food grains had contrasting effects on the bioaccessibility of zinc and iron. Zinc bioaccessibility of chickpea was not affected while it was significantly decreased in the case of finger millet (up to 38%) and green gram (up to 44%). Iron bioaccessibility increased by 62% in green gram, by 39% in chickpea and by 20% in finger millet after germination. Platel, Eipeson and Srinivasan (2010) observed as well that in general the impact of germination on zinc bioaccessibility is much lower (or even negative) compared to the one observed for iron.

4.6 Thermal processing

The previously described processing techniques are mainly applied on pulses and cereal grains. Heat treatments, such as cooking, pasteurization, sterilization, microwave heating and roasting, are more widely used. These techniques all differ in temperature-time profiles obtained during the process, as well as by the use of dry or wet heating technologies (Wang and Sun 2016).

Since minerals are heat-stable, they will not be destroyed during the treatment, but they can leach out if wet heating is performed (Schroeder 1971). In addition, in the case of wet heat treatments, heat-stable antinutrients such as phytic acid and polyphenols (predominant in seed coats and outer layers) can leach out as well (Wang et al. 2010). Rehman and Shah (2005) reported for pulses a reduction of about 21-27% tannin and 24-35% phytic acid contents upon cooking. The reduction of phytic acid and tannin has been shown to increase mineral bioaccessibility and bioavailability (Disler et al. 1975; Brune, Rossander and Hallberg 1989; Hurrell, Reddy and Cook 1999; Layrisse et al. 2000; Petry et al. 2010; Gupta, Gangoliya and Singh 2015). Dietary fiber has shown to be effected by thermal processing (Dhingra et al. 2012). In general, heat treatments can change the ratio between insoluble and soluble fibers as

well as the total dietary fiber content (Elleuch et al. 2011). However, no clear statement upon fiber increase or decrease during thermal treatment can be made due to conflicting results in current literature. On the one hand, Rehman and Shah (2004) reported, for example, a decrease of insoluble dietary fiber components (e.g. cellulose and hemicellulose) after cooking pre-soaked pulses. Reduction of these components could be attributed to partial degradation of cellulose and hemicellulose into simple carbohydrates (e.g. glucose, arabinose, xylose and galactose) since an increased temperature has been reported to split glycoside linkages in dietary fiber polysaccharides (Nyman and Asp 1987). On the other hand, cooking significantly increased the insoluble dietary fiber fraction for all pulses studied by Wang et al. (2010). This increase may be due to formation of protein-fiber complexes after Maillard reactions, induced by the cooking process, in which carbohydrates and proteins condense to form insoluble polymers (e.g. lignin) (Van Soest and Robertson 1979). Changes in soluble dietary fiber content, as a consequence of thermal treatment, can be due to leaching in the cooking media (causing a decrease) and formation of resistant starch and Maillard reaction products (causing an increase) (Van Soest and Roberson 1979; Osorio-Diaz et al. 2003; Dhingra et al. 2012). Moreover, more soluble fiber is expected to leach out after thermally induced depolymerization of the fiber. Upon depolymerization, caused by heat processing of plant-based foods, soluble dietary fiber shows a shift towards a lower molecular weight (Sila et al. 2009). When pectin is depolymerized, it is believed that the mineral binding capacity will be reduced (Kyomugasho et al. 2018). Because of these contradictory phenomena, studies reported decreasing, increasing and non-changing soluble dietary fiber fractions in plant-based foods after thermal treatment. In legumes and cereals, both decrease and increase of soluble dietary fiber has been reported. For example, Kutos et al. (2003) studied the modifications that happen during the thermal processing of kidney beans and reported that total fibre content was reduced mainly due to loss of soluble fibre. However, Puna and Paruchuri (2004) did not see a significant change on the

total, soluble and insoluble dietary fiber contents in green leafy vegetables upon cooking. Mainly a changing soluble dietary fiber content is believed to affect the mineral bioaccessibility and bioavailability of plant-based foods since the mineral binding capacity of insoluble dietary fibers is negligible (Persson et al. 1987). However, an effect on mineral bioaccessibility caused by changes in soluble and insoluble dietary fiber content (due to thermal processing) still should be confirmed by research.

Thermal processing has also the potential to enhance mineral bioaccessibility and bioavailability by releasing them from entrapment in the plant matrix, by influencing several physical barriers in plant-based foods. On the one hand, food processing by heat can generally alter bioaccessibility and bioavailability of macronutrients (Hemalatha, Platel and Srinivasan 2007). Depending on starch type and type of heat treatment, gelatinization may occur (Ma et al. 2011). Since gelatinized starch is more susceptible to α -amylase, this form of starch is more easily digestible (Batey 1982). Besides, protein denaturation, which enhances protein digestibility, can occur during thermal processing (Davis and Williams, 1998). This implies that thermal processing can have a positive influence on mineral bioaccessibility and bioavailability if, as mentioned in §3.2, it is hypothesized that undigested macronutrients, surrounding minerals, can form a physical barrier for mineral transfer to the absorption site in the small intestine. Moreover, since protein digestibility increases when food is heated, protein-bound elements can be released which can improve the absorption of these micro-elements (Oliveira et al. 2018). On the other hand, heat processing can also alter the plant cell wall structure, cell wall softening and disruption. This effect can mainly be attributed to solubilization and depolymerization of pectin in the middle lamella (Sila et al. 2009; Njoroge et al. 2016). As a consequence, the adhesion between surrounding cells is reduced which facilitates the release of intact cells upon mechanical stress (e.g. grinding or chewing) (Dhital et al. 2016; Pallares et al. 2018). If during mechanical stress cells are separated instead of

broken down, the cell content cannot be released and the cell wall can remain a physical barrier for mineral release and absorption. However, if during processing the cell wall becomes permeable (as pectin is solubilized), it is expected that small molecules and compounds can still be released. Because of this phenomena, the sequence of processing techniques can be of relevance. For example, if pulse seeds are grinded before thermal processing, the cell wall as a physical barrier will be eliminated and cell content will be released. However, if pulse seeds are first thermally processed, grinding will lead to cell separation and the (more permeable) cell wall can nevertheless still remain a physical barrier.

In addition, depending on the heat treatment, enzymes will be inactivated in most cases. As a consequence, phytase for example, will no longer contribute to the enhancement of mineral bioaccessibility and bioavailability (Raes et al. 2014).

In general, thermal processing can influence mineral bioaccessibility and bioavailability in several ways. The interplay between these factors makes investigating the effect of thermal processing a complex matter, therefore further research is needed.

5. Conclusions and future outlook

The reduced iron and zinc bioaccessibility and bioavailability from plant-based foods can be attributed to several inherent factors such as the presence of mineral antinutrients and physical barriers. Insoluble and non-absorbable mineral chelates, formed with dietary fiber, phytic acid, and some polyphenols in the plant-based food system or in the digestive tract cannot be broken down during human digestion and consequently, they cannot be absorbed in the small intestine. In addition, minerals which are bound to absorbable polyphenols are generally not released during the polyphenol metabolism. Among dietary fibers, mostly soluble dietary fiber (such as pectin) negatively influences iron and zinc absorption. The binding strength of minerals for phytic acid is proportional to their atomic mass and electronegativity. Therefore, zinc has been

shown to form stronger complexes with phytic acid than lighter atoms, such as iron. As a result, phytic acid negatively impacts zinc absorption at lower concentrations compared to iron absorption. In the case of polyphenols, mainly iron absorption is inhibited.

The quest of why mineral bioaccessibility and bioavailability is reduced in plant-based food systems is an intricate matter. In reality, the reduced mineral bioaccessibility and bioavailability can never be attributed to a single factor only, for example, there is always competition at several levels inside a plant-based food system. Minerals are involved in mutual competition to bind antinutrients, while antinutrients compete each other to bind minerals. Moreover, as mentioned before, an antinutrient can be bound to another antinutrient (e.g. phytic acid and polyphenols to dietary fiber) which should be kept in mind when investigating reduced mineral bioaccessibility and bioavailability in plant-based food systems. Furthermore, mineral antinutrients can also form insoluble complexes with dietary proteins, starch and other carbohydrates, reducing their digestibility as well. It becomes even more complicated since minerals and the mineral chelates are embedded in a food matrix, surrounded by macronutrients and a cell wall, forming physical barriers. Overall, the interplay between antinutrients, minerals and other factors creates a very complex system, playing an essential part in the understanding of mineral bioaccessibility and bioavailability in real food systems.

The positive effect of different processing techniques on mineral bioaccessibility and bioavailability of plant-based foods, mostly relies on the fact that the amount of antinutrients is reduced due to the removal of fractions rich in antinutrients and/or due to their leaching into the processing liquid. In addition, activation of enzymes (e.g. phytase) can enhance mineral bioaccessibility and bioavailability. Although processing can have a positive effect, it also can induce a reduced mineral concentration and mineral bioaccessibility and bioavailability (e.g. leaching out minerals, cell wall intactness when grinding is applied after cooking, phytase inactivation during thermal processing).

Breeding programs to grow new varieties with lower antinutrient levels can also be a solution, besides reducing antinutrient content through processing. However, the function that mineral antinutrients have in plants, should not be forgotten. In addition, it should be taken into account that mineral antinutrients can possess other health-promoting effects as well.

Challenges in investigating mineral bioaccessibility and bioavailability in plant-based foods and how this can be influenced by food processing, not only include the complexity of the interplay between all the possible barriers but also include strategic choices that need to be taken in the context of the relevant experimental set up for the investigation of this problem. Nowadays, mineral bioaccessibility is mainly evaluated by *in vitro* methods. They offer a standardized, high-throughput screening method that may predict mineral bioaccessibility. By expanding these methods with, for example, relevant cell lines, an idea on nutrient bioavailability can be given. Nevertheless, estimating nutrient bioavailability in foods ideally should be determined by *in vivo* studies, taking into account the whole range of nutritional, physiological and ecological factors that can influence absorption (Guéguen & Pointillart, 2000). Therefore, *in vitro* methods should be seen as good screening methods, but validation by *in vivo* methods is necessary. However, nowadays it is still difficult to examine long term and between- and inter-person variations effects by *in vivo* methods. In addition, there is a need to investigate the specific role of the gut microflora on mineral release and to what extend minerals are functionalised in the colon. Furthermore, researchers should not only focus on pulses and cereal for investigating this matter (which mainly has been done now), but should also include more often other plant-based foods such as fruit and vegetables, which might not be best plant-based sources for minerals but might be rich in relevant antinutrients as well.

References

- Afify, A.E.M.M.R., El-Beltagi, H.S., El-Salam, S.M.A. and Omran, A.A. (2011). Bioavailability of iron, zinc, phytate and phytase activity during soaking and germination of white sorghum varieties. *PLoS ONE* **6**: e25512.
- Albarracín, M., González, R.J. and Drago, S.R. (2013). Effect of soaking process on nutrient bio-accessibility and phytic acid content of brown rice cultivar. *LWT-Food Sci. Technol.* **53**: 76-80.
- Alegria, A., Cilla, A., Farré, R. and Lagarda, M.J. (2015). Inorganic Nutrients. **In**: Handbook of Food Analysis (3rd ed.). pp. 733-753. Nollet, L.M.L. and Toldra, F., Eds., CRC Press, Taylor and Francis Group, LLC.
- Andrews, M., Briones, L., Jaramillo, A., Pizarro, F. and Arredondo, M. (2014). Effect of calcium, tannic acid, phytic acid and pectin over iron uptake in an in vitro Caco-2 cell model. *Biol. Trace Elem. Res.* **158**: 122–127.
- Bailey, R.L., West, K.P. and Black, R.E. (2015). The epidemiology of global micronutrient deficiencies. *Ann. Nutr. Metab.* **66**: 22–33.
- Basu, T.K. and Donaldson, D. (2003). Intestinal absorption in health and disease: micronutrients. *Best Pract. Res. Cl. Ga.* **17**: 957-979.
- Batey, I.L. (1982). Starch analysis using thermostable alpha-amylases. *Starch* **34**: 125-128.
- Baye, K., Guyot, J.P. and Mouquet-Rivier, C. (2017). The unresolved role of dietary fibers on mineral absorption. *Crit. Rev. Food Sci.* **57**: 949–957.
- Belderok, B., Mesdag, J. and Donner, D.A. (2000). Milling of wheat. **In**: Bread-making quality of wheat. Pp. 21-29. Springer Science+Business Media Dordrecht.
- Belitz, H.D., Grosch, W. and Schieberle, P. (2009). Food chemistry. Springer-Verlag, Berlin Heidelberg.
- Berdanier, C.D., Dwyer, J.T. and Heber, D. (2013). Handbook of nutrition and food (3rd ed.). CRC Press, Taylor and Francis Group, LLC.
- Bielsalski, H.K. (2013). Hidden Hunger. Springer-Verlag, Berlin Heidelberg.
- Black, R.G., Singh, U. and Meares, C. (1998). Effect of genotype and pretreatment of field peas (*Pisum sativum*) on their dehulling and cooking quality. *J. Sci. Food Agric.* **77**: 251-258.
- Bohn, L., Meyer, S.A. and Rasmussen, K. (2008). Phytate: impact on environment and human nutrition. A challenge for molecular breeding. *J Zhejiang Univ Sci B.* **9**: 165-191.
- Boland, M., Golding, M. and Singh, H. (2014). Food structures, Digestion and Health. Academic Press, Elsevier Inc.

792 Bosscher, D., Van Caillie-Bertrand, M., Van Cauwenbergh, R. and Deelstra, H. (2003).
 793 Availabilities of calcium, iron, and zinc from dairy infant formulas is affected by soluble
 794 dietary fibers and modified starch fractions. *Nutrition*. **19**: 641–645.

795 Bravo, L. (1998). Polyphenols : Chemistry, dietary sources, metabolism and nutritional
 796 significance. *Nutr. Rev.* **56**: 317–333.

797 Brune, M., Rossander, L. and Hallberg, L. (1989). Iron absorption and phenolic compounds:
 798 importance of different phenolic structures. *Eur. J. Clin. Nutr.* **43**: 547–58.

799 Burton, R.A., Gidley, M.J. and Fincher, G.B. (2010). Heterogeneity in the chemistry,
 800 structure and function of plant cell walls. *Nat. Chem. Biol.* **6**: 724-732.

801 Burton, R.A. and Fincher, G.B. (2014). Evolution and development of cell walls in cereal
 802 grains. *Front. Plant Sci.* **5**: 456.

803 Caffall, K.H. and Mohnen, D. (2009). The structure, function, and biosynthesis of plant cell
 804 wall pectic polysaccharides. *Carbohydr. Res.* **344**: 1879-1900.

805 Camire, A.C. and Clydesdale, F.M. (1981). Effect of pH and heat treatment on the binding of
 806 calcium, magnesium, zinc, and iron, to wheat bran and fractions of dietary fiber. *J. Food.*
 807 *Sci* **46**: 548-557.

808 Celus, M., Kyomugasho, C., Salvia-Trujillo, L., Van Audenhove, J., Van Loey, A.M.,
 809 Grauwet, T. and Hendrickx, M.E. (2018). Interactions between citrus pectin and Zn²⁺ or
 810 Ca²⁺ and associated in vitro Zn²⁺ bioaccessibility as affected by degree of
 811 methylesterification and blockiness. *Food Hydrocolloids* **79**: 319-330.

812 Chan, S.Y., Choo, W.S., Young, D.J. and Loh, X.J. (2017). Pectin as a rheology modifier:
 813 Origin, structure, commercial production and rheology. *Carbohydr. Polymers* **161**: 118–
 814 139.

815 Chigwedere, C. M., Nkonkola, C. M., Kyomugasho, C., Jamsazzadeh Kermani, Z., Pallares
 816 Pallares, A., Van Loey, A. M., Grauwet, T. and Hendrickx, M. E. Cotyledon pectin
 817 molecular interconversions rather than cation-mediated crosslinking during aging
 818 explain pectin solubilization kinetics upon cooking of Canadian wonder (*Phaseolus*
 819 *vulgaris*) beans. Submitted to Food Hydrocolloids.

820 Considine, K.M., Kelly, A.L., Fitzgerald, G.F., Hill, C. and Sleator, R.D. (2008). High-
 821 pressure processing – effects on microbial food safety and food quality. *FEMS*
 822 *Microbiol. Lett.* **281**: 1-9.

823 Coudray, C., Bellanger, J., Castiglia-Delavaud, C., Remesy, C., Vermorel, M. and
 824 Rayssiguier, Y. (1997). Effect of soluble or partly soluble dietary fibres
 825 supplementation on absorption and balance of calcium, magnesium, iron and zinc in
 826 healthy young men. *Eur. J. Clin. Nutr.* **51**: 375–380.

827 Coudray, C., Bousset, C., Pépin, D., Tressol, J. C., Bellanger, J. & Rayssiguier, Y. (1998)
 828 Short-term ingestion of chlorogenic or caffeic acids decreases zinc but not copper
 829 absorption in rats, utilisation of stable isotopes and inductively coupled plasma mass
 830 spectrometry technique. *Br. J. Nutr.* **80**: 575-584.

831 Coudray, C., Tressol, J.C., Feillet-Coudray, C., Bellanger, J., Pépin, D. and Mazur, D. (2000).
832 Long-term consumption of red wine does not modify intestinal absorption or status of
833 zinc and copper in rats. *J. Nutr.* **5**: 1309-1313.

834 Coudray, C., Tressol, J.C., Gueux, E. and Rayssiguier, Y. (2003). Effects of inulin-type
835 fructans of different chain length and type of branching on intestinal absorption and
836 balance of calcium and magnesium in rats. *Eur. J. Nutr.* **42**: 91–98.

837 Crook, M.A. (2011). Zinc deficiency. *Nutrition.* **27**: 1085–1086.

838 de Almeida Costa, G.E., Queiroz-Monici K.S., Machado Reis, S.M.P. and de Oliveira, A.C.
839 (2006). Chemical composition, dietary fibre and resistant starch contents of raw and
840 cooked pea, common bean, chickpea and lentil legumes. *Food Chem.* **94**: 327-330.

841 Debon, S.J.J. and Tester, R.F. (2001). In vitro binding of calcium, iron and zinc by non-starch
842 polysaccharides. *Food Chem.* **73**: 401-410.

843 Delzenne, N., Aertssens, J., Vreplaetse, H., Roccaro, M. and Robefroid, M. (1995). Effect of
844 fermentable fructo-oligosaccharides on mineral, nitrogen and energy digestive balance in
845 the rat. *Life Sci.* **57**: 1579–1587.

846 Diaz, A.M., Caldas, G.V. and Blair, M.W. (2010). Concentrations of condensed tannins and
847 anthocyanins in common bean seed coats. *Food Res. Int.* **43**: 595-601.

848 Dhingra, D., Michael, M., Rajput, H. and Patil, R.T. (2012). Dietary fibre in foods: a review.
849 *J. Food Sci. Technol.* **49**: 255-266.

850 Dhital, S., Bhattarai, R.R., Gorham, J. and Gidley, M.J. (2016). Intactness of cell wall
851 structure controls the in vitro digestion of starch in legumes. *Food Funct.* **7**: 1367-1379.

852 Disler, P.B., Lynch, S.R., Charlton, R.W., Torrance, J.D., Bothwell, T.H., Walker, R.B. and
853 Mayet, F. (1975). The effect of tea on iron absorption. *Gut.* **16**: 193–200.

854 Drews L.M., Kies C. and Fox M. (1979). Effect of dietary fiber on copper, zinc and
855 magnesium utilisation by adolescent boys. *Am. J. Clin. Nutr.* **32**: 1893-1897.

856 Ducros, V., Arnaud, J., Tahiri, M., Coudray, C., Bornet, F., Bouteloup-Demange, C., Brouns,
857 F., Rayssiguier, Y. and Roussel, A.M. (2005). Influence of short-chain fructo-
858 oligosaccharides (sc-FOS) on absorption of Cu, Zn, and Se in healthy postmenopausal
859 women. *J. Am. Coll. Nutr.* **24**: 30–37.

860 Duhan, A., Khetrappaul, N. and Bishnoi, S. (2004). HCl – extractability of zinc and copper as
861 affected by soaking, dehulling, cooking and germination of high yielding pigeon pea
862 cultivars. *J. Food Comp. Anal.* **17**: 597–604.

863 Dykes, L. and Rooney, W. (2007). Phenolic compounds in cereal grains and their health
864 benefits. *Cereal Food. World* **52**: 105-111.

865 Eagling, T. Neal, A.L., Mcgrath, S.P., Fairweather-Tait, S., Shewry, P.R., Zhao, F-J.
866 Distribution and speciation of iron and zinc in grain of two wheat genotypes. *J. Agricul.*
867 *Food Chem.* **62**:708-716.

868 Eashwarage, I.S., Herath, H.M.T. and Gunathilake, K.G.T. (2017). Dietary fiber, resistant
869 starch and *in vitro* starch digestibility of selected eleven commonly consumed legumes
870 (Mung bean, Cowpea, Soybean and Horse Gram) in Sri Lanka. *Res. J. Chem. Sci.* **7**: 1-7.

871 Ellegard, L., Andersson, H. and Bosaeus, I. (1997). Inulin and oligofructose do not influence
872 the absorption of cholesterol, or the excretion of cholesterol, Ca, Mg, Zn, Fe, or bile
873 acids but increases energy excretion in ileostomy subjects. *Eur. J. Clin. Nutr.* **51**: 1-5.

874 Elleuch, M., Bedigian, D., Roiseux, O., Besbes, S., Blecker, C. and Attia, H. (2011). Dietary
875 fibre and fibre-rich by-products of food processing: Characterisation, technological
876 functionality and commercial applications: A review. *Food Chem.* **124**: 411-421.

877 Eskin, N.A.M. and Shahidi, F. (2013). Biochemistry of foods (3rd ed.). Academic Press,
878 Elsevier Inc.

879 Eyzaguirre, R.Z., Nienaltowska, K., de Jong, L.E.Q., Hasenack, B.B.E. and Nout, M.J.R.
880 (2006). Effect of food processing of pearl millet (*Pennisetum glaucum*) IKMP-5 on the
881 level of phenolics, phytate, iron and zinc. *J. Sci. Food Agr.* **86**: 1391-1398.

882 FAO & World Health Organization (2004). Vitamin and mineral requirements in human
883 nutrition Second edition. World Health Organization, 1–20.

884 Fardet, A. (2010). New hypotheses for the health-protective mechanisms of whole-grain
885 cereals: What is beyond fibre? *Nutr. Res. Rev.* **23**: 65–134.

886 Fernandez, R. and Phillips, S. (1982). Components of fiber bind iron in vitro. *Am. J. Clin.*
887 *Nutr.* **35**: 100–106.

888 Fernández-García, E., Carvajal-Lérída, I. and Pérez-Gálvez, A. (2009). In vitro
889 bioaccessibility assessment as a prediction tool of nutritional efficiency. *Nutr. Res.* **29**:
890 751-760.

891 Figuerola, F., Hurtado, M.L., Estevez, A.M., Chiffelle, I. and Asenjo, F. (2005). Fibre
892 concentrates from apple pomace and citrus peel as potential fibre sources for food
893 enrichment. *Food Chem.* **91**: 395–401.

894 Fraga, C.G., Galleano, M., Verstraeten, S.V. and Oteiza, P.I. (2010). Basic biochemical
895 mechanisms behind the health benefits of polyphenols. *Mol. Aspects Med.* **31**: 435-445.

896 Frossard, E., Bucher, M., Mächler, F., Mozafar, A. and Hurrell, R. Potential for increasing
897 the content and bioavailability of Fe, Zn and Ca in plants for human nutrition. *J. Sci.*
898 *Food Agric.* **80**: 861-879.

899 Fuqua, B.K., Vulpe, C.D. and Anderson, G.J. (2012). Intestinal iron absorption. *J. Trace*
900 *Elem. Med. Bio.* **26**: 115-119.

901 Ganji, V. and Kies, C.V. (1994). Zinc bioavailability and tea consumption: studies in healthy
902 humans consuming self-selected and laboratory-controlled diets. *Plant Food Hum. Nutr.*
903 **46**: 267-276.

904 Ganong, W.F. (1995). Review of medical physiology. LANGE Medical Publications/Los
905 Altos, California.

- 906 Garcia-Lopez, J. and Lee, K. (1985). Iron binding by fiber is influenced by competing
907 minerals. *Am. J. Physiol.* **250**: 420-426.
- 908 Ghavidel, R.A. and Prakash, J. (2007). The impact of germination and dehulling on nutrients,
909 antinutrients, in vitro iron and calcium bioavailability and in vitro starch and protein
910 digestibility of some legume seeds. *LWT-Food Sci Technol.* **40**: 1292-1299.
- 911 Gibson RS, Hotz C (2001). Dietary diversification/modification strategies to enhance
912 micronutrient content and bioavailability of diets in developing countries. *Br. J. Nutr.*
913 **85**: 159–166.
- 914 Gibson, R.S., Bailey, K.B., Gibbs, M. and Ferguson, E.L. (2010). A review of phytate, iron,
915 zinc, and calcium concentrations in plant-based complementary foods used in low-
916 income countries and implications for bioavailability. *Food Nutr. Bull.* **31**: 134-146.
- 917 Glahn, R.P., Tako, E., Cichy, K. and Wiesinger, J. (2016). The cotyledon cell wall and
918 intracellular matrix are factors that limit iron bioavailability of the common bean
919 (*Phaseolus vulgaris*). *Food Funct.* **7**: 3193–3200.
- 920 Glahn, R.P., Wortley, G.M., South, P.K. and Miller, D.D. (2002). Inhibition of iron uptake by
921 phytic acid, tannic acid, and ZnCl₂: studies using an *in vitro* digestion/Caco-2 cell model.
922 *J. Agric. Food Chem.* **50**: 390-395.
- 923 Gopalsamy, G.L., Alpers, D.H., Binder, H.J., Tran, C.D., Ramakrishna, B.S., Brown, I.,
924 Manary, M., Mortimer, E. and Young, G.P. (2015). The relevance of the colon to zinc
925 nutrition. *Nutrients* **7**: 572-583.
- 926 Graf, E. and Eaton, J.W. (1985). Dietary suppression of colonic cancer fiber or phytate?
927 *Cancer* **56**: 717-718.
- 928 Greger, J.L. (1999). Nondigestible Carbohydrates and Mineral Bioavailability. *J. Nutr.* **129**:
929 1418–1423.
- 930 Gregory, P.J., Wahbi, A., Adu-Gyamfi, J., Heiling, M., Gruber, R., Joy, E.J.M. and Broadley,
931 M.R. (2016). Approaches to reduce zinc and iron deficits in food systems. *Glob. Food*
932 *Secur.* In press.
- 933 Guéguen, L. and Pointillart, A. (2000). The bioavailability of dietary calcium. *J. Am. Coll.*
934 *Nutr.* **19**: 119-136.
- 935 Guillon, F. and Champ, M. (2000). Structural and physical properties of dietary fibres, and
936 consequences of processing on human physiology. *Food Res. Int.* **33**: 233–245.
- 937 Gupta, R.K., Gangoliya, S.S. and Singh, N.K. (2015). Reduction of phytic acid and
938 enhancement of bioavailable micronutrients in food grains. *J. Food Sci. Technol.* **52**:
939 676-684.
- 940 Hallberg, L., Brune, M. and Rossander, L. (1989). Iron absorption in man: ascorbic acid
941 and dose-dependent inhibition by phytate. *Am. J. Clin. Nutr.* **49**: 140–144.
- 942 Haslam, E. (1992). Gallic acid and its metabolites. In: Plant polyphenols, pp. 169-194.
943 Hemmingway, R.W. and Laks, P.E., Eds., Plenum Press, New York.

- 944 Hayashi, T. (2006). The science and lore of the plant cell wall: biosynthesis, structure and
945 function. Florida, BrownWalker Press.
- 946 Hayat, I., Ahmad, A., Masud, T., Ahmed, A. and Bashir, S. (2014). Nutritional and health
947 perspectives of beans (*Phaseolus vulgaris* L.): an overview. *Crit. Rev. Food Sci. Nutr.*
948 **54**: 580–92.
- 949 Hentze, M.W., Muckenthaler, M.U., Galy, B. and Camaschella, C. (2010). Two to tango:
950 regulation of Mammalian iron metabolism. *Cell*. **142**: 24-38.
- 951 Hemalatha, S., Platel, K. and Srinivasan, K. (2007). Influence of germination and
952 fermentation on bioaccessibility of zinc and iron from food grains. *Eur. J. Clin. Nutr.* **62**:
953 342-348.
- 954 Hipsley, E.H., 1953. Dietary “fibre” and pregnancy toxemia. *Brit. Med. J.* **2**: 420–422.
- 955 Holzapfel, W. H. (2002). Appropriate starter culture technologies for small scale
956 fermentation in developing countries. *Int. J. Food Microbiol.* **75**: 197-212.
- 957 Hunt, J.R. (2003). Bioavailability of iron, zinc, and other trace minerals from vegetarian
958 diets. *Am. J. Clin. Nutr.* **78**: 633-639.
- 959 Hurrell, R. and Egli, I. (2010). Iron bioavailability and dietary reference values. *The Am. J.*
960 *Clin. Nutr.* **91**: 1461–1467.
- 961 Hurrell, R.F., Juillerat, M.A., Reddy, M., Lynch, S.R., Dassenko, S.A. and Cook, J.D. (1992).
962 Soy protein, phytate and iron adsorption in humans. *Am. J. Clin. Nutr.* **56**: 573-578.
- 963 Hurrell, R.F., Reddy, M. and Cook, J.D. (1999). Inhibition of non-haem iron absorption in
964 man by polyphenolic-containing beverages. *Brit. J. Nutr.* **81**: 289-295.
- 965 Hurrell, R.F., Reddy, M., Juillerat, M.A. and Cook, J.D. (2003). Degradation of phytic acid in
966 cereal porridges improves iron absorption by human subjects. *Am. J. Clin. Nutr.* **77**:
967 1213-1219.
- 968 Idouraine, A., Hassani, B.Z., Claye, S.S. and Weber, C.W. (1995). In vitro binding capacity
969 of various fiber sources for magnesium, zinc and copper. *J. Agr. Food Chem.* **43**: 1580–
970 1584.
- 971 Iffat, A.T.K., Maqsood, Z.T. and Fatima, N. (2005). Study of complex formation of Fe(III)
972 with tannic acid. *J. Chem. Soc. Pakistan.* **27**: 174–177.
- 973 Jackson, A.D. and McLaughlin, J. (2009). Digestion and absorption. *Surgery* **27**: 231-2316.
- 974 Jenab, M. and Thompson, L.U. (2001). Role of phytic acid in cancer and other diseases. **In**:
975 Food phytates, pp. 225-248. Reddy, N.R. and Sathe, S.K., Eds., CRC Press, Taylor &
976 Francis Group, Boca Raton.
- 977 Joint FAO/WHO Food Standards Programme Commision (2016). CODEX Alimentarius
978 (CODEX) Guidelines on Nutrition Labelling CAC/GL 2-1985 as Last Amended 2016,
979 Rome.

980 Karamać, M. (2009). Chelation of Cu(II), Zn(II), and Fe(II) by tannin constituents of selected
981 edible nuts. *Int. J. Mol. Sci.* **10**: 5485–5497.

982 Kayodé, A.P., Mertz, C., Guyot, J.P., Brat, P. and Mouquet-Rivier, C. (2013). Fate of
983 phytochemicals during malting and fermentation of type III tannin sorghum and impact
984 on product biofunctionality. *J. Agr. Food Chem.* **61**: 1935-1942.

985 Khandelwal, S., Udipi, S.A. and Ghugre, P. (2010). Polyphenols and tannins in Indian pulses:
986 Effect of soaking, germination and pressure cooking. *Food Res. Int.* **43**: 526-530.

987 Khattab, R.Y. and Arntfield, S.D. (2009). Nutritional quality of legume seeds as affected by
988 some physical treatments 2. Antinutritional factors. *LWT-Food Sci. Technol.* **42**: 1113-
989 1118.

990 Kim, M., Atallah, M. T., Amarasiriwardena, C. and Barnes, R. (1996). Pectin with low
991 molecular weight and high degree of esterification increases absorption of ⁵⁸Fe in
992 growing rats. *J. Nutr.* **126**: 1883-1890.

993 Kohajdova, A. and Karovicova, J. (2007). Fermentation of cereals for specific purpose. *J.*
994 *Food Nutr. Res.* **46**: 51-57.

995 Konietzny, U. and Greiner, R. (2002). Molecular and catalytic properties of phytate-
996 degrading enzymes (phytases). *Int. J. Food Sci. Technol.* **37**: 791-812.

997 Krebs, N.F. (2000). Overview of zinc absorption and excretion in the human gastrointestinal
998 tract. *J. Nutr.* **130**: 1374-1377.

999 Kruger, J., Taylor, J.R., Du, X., De Moura, F.F., Lönnnerdal, B. and Oelofse, A. (2013). Effect
1000 of phytate reduction of sorghum, through genetic modification, on iron and zinc
1001 availability as assessed by an in vitro dialysability bioaccessibility assay, Caco-2 cell
1002 uptake assay, and suckling rat pup absorption model. *Food Chem.* **141**: 1019–1025.

1003 Kumar, V., Sinha, A.K., Makkar, H.P.S. and Becker, K. (2010). Dietary roles of phytate and
1004 phytase in human nutrition: A review. *Food Chem.* **120**: 945–959.

1005 Kutos, T., Golob, T., Kac, M. and Plestenjak, A. (2003). Dietary fibre content of dry and
1006 processed beans. *Food Chem.* **80**: 231-235.

1007 Kyomugasho, C., Gwala, S., Christiaens, S., Kermani, J.Z., Van Loey, A., Grauwet, T. and
1008 Hendrickx, M. (2017). Pectin nanostructure influences pectin-cation interactions and in
1009 vitro-bioaccessibility of Ca²⁺, Zn²⁺, Fe²⁺ and Mg²⁺-ions in model systems. *Food*
1010 *Hydrocolloids* **62**: 299-310

1011 Kyomugasho, C., Munyensanga, C., Celus, M., Van de walle, D., Dewittinck, K., Van Loey,
1012 A.M., Hendrickx, M. and Grauwet, T. (2018). Molar mass influence on pectin-Ca²⁺
1013 adsorption capacity, interaction energy and associated functionality: gel micro structure
1014 and stiffness. Submitted to Food Hydrocolloids.

1015 Kyomugasho, C., Willemsen, K., Christiaens, S., Van Loey, A. and Hendrickx, M. (2015).
1016 Pectin-interactions and in vitro bioaccessibility of calcium and iron in particulated
1017 tomato-based suspensions. *Food Hydrocolloids* **49**: 164-175.

- 1018 Larsson, M., Rossander-Hulten, L., Sandstrom, B. and Sandberg, A. (1996). Improved zinc
1019 and iron absorption from breakfast meals containing malted oats with reduced phytate
1020 content. *Br. J. Nutr.* **76**: 677-688.
- 1021 Layrisse, M., Garcia-Casal, M.N., Solano, L., Baron, M.A., Arguello, F., Llovera, D.,
1022 Ramirez, J., Leets, I. and Tropper, E. (2000). Iron bioavailability in humans from
1023 breakfasts enriched with iron bis-glycine chelate, phytates and polyphenols. *J. Nutr.* **130**:
1024 2195-2199.
- 1025 Lestienne, I., Besancon, P., Caporiccio, B., Lullien-Pellerin, V. and Tréche, S. (2005). Iron
1026 and zinc in vitro availability in pearl millet flours (*Pennisetum glaucum*) with varying
1027 phytate, tannin, and fiber contents. *Agr. Food Chem.* **53**: 3240–3247.
- 1028 Lestienne, I., Buisson, M., Mullien-Pellerin, V., Picq, C. and Treche, S. (2007). Losses of
1029 nutrients and antinutritional factors during abrasive decortication of two pearl millet
1030 cultivars (*Pennisetum glaucum*). *Food Chemistry*, 100, 1316-1323.
- 1031 Lestienne, I., Icard-Vernière, C., Mouquet, C., Picq, C. and Trèche, S. (2005). Effects of
1032 soaking whole cereal and legume seeds on iron, zinc and phytate contents. *Food Chem.*
1033 **89**: 421–425.
- 1034 Liang, J., Han, B.H., Nout, M.J.R. and Hamer, R.J. (2008). Effects of soaking, germination
1035 and fermentation on phytic acid, total and in vitro soluble zinc in brown rice. *Food*
1036 *Chem.* **110**: 821-828.
- 1037 Liu, X., Kim, J., Li, Y., Li, J., Liu, F. and Chen, X. (2005). Tannic acid stimulates glucose
1038 transport and inhibits adipocyte differentiation in 3T3-L1 cells. *J. Nutr.* **135**: 165-171.
- 1039 Lobo, A.R., Filho, J.M., Alvares, E.P., Cocato, M.L. and Colli, C. (2009). Effects of dietary
1040 lipid composition and inulin-type fructans on mineral bioavailability in growing rats.
1041 *Nutrition.* **25**: 216–225.
- 1042 Lopez, H. and Leenhardt, F. (2002). Minerals and phytic acid interactions: is it a real problem
1043 for human nutrition? *Int. J. Food Sci. Tech.* **37**: 727–739.
- 1044 Luo, Y. and Xie, W. (2012). Effect of phytase treatment on iron bioavailability in faba bean
1045 (*Vicia faba* L.) flour. *Food Chem.* **134**: 1251–1255.
- 1046 Luo, Y., Xie, W and Cui, Q. (2010). Effects of Phytases and Dehulling Treatments on In Vitro
1047 Iron and Zinc Bioavailability in Faba Bean (*Vicia faba* L.) Flour and Legume Fractions.
1048 *J. Food Sci.* **75**: 191-198.
- 1049 Ma, G. (2007). Iron and zinc deficiencies in China: Existing problems and possible solutions.
- 1050 Ma, Z., Boye, J.I., Simpson, B.K., Prasher, S.O., Monpetit, D. and Malcolmson, L. (2011).
1051 Thermal processing effects on the functional properties and microstructure of lentil,
1052 chickpea and pea flours. *Food Res. Int.* **44**: 2534-2544.
- 1053 Mahgoub, S.E.O. and Elhag, S.A. (1998). Effect of milling, soaking, malting, heat-treatment
1054 and fermentation on phytate level of four Sudanese sorghum cultivars. *Food Chem.* **61**:
1055 77-80.

- 1056 Manary, M.J., Hotz, C., Krebs, N.F., Gibson, R.S., Westcott, J.E., Arnold, T., Broadhead,
1057 R.L. and Hambridge, K.M. (2000). Dietary phytate reduction improves zinc absorption
1058 in Malawian children recovering from tuberculosis but not in well children. *J. Nutr.* **130**:
1059 2959-2964.
- 1060 Mennen, L.I., Walker, R., Bennetau-Pelissero, C., Scalbert, A., 2005. Risks and safety of
1061 polyphenol consumption. *Am. J. Clin. Nutr.* **81**: 326-329.
- 1062 Miller, D. (1996). Minerals. **In**: Food Chemistry. Fennema, O.R., Ed., Marcel Dekker, Inc.,
1063 New York.
- 1064 Mira, L., Fernandez, M.T., Santos, M., Rocha, R., Florencio, M.H. and Jennings, K.R.
1065 (2002). Interactions of flavonoids with iron and copper ions: a mechanism for their
1066 antioxidant activity. *Free Radical Res.* **36**: 1199–1208.
- 1067 Mishra, S., Hardcare, A. and Monro, J. (2010). Food structure and carbohydrate digestibility.
1068 **In**: Carbohydrates – Comprehensive studies on glycobiology, pp. 289-316. Chang, C.F.,
1069 Ed., InTech, Croatia.
- 1070 Miyada, T., Nakajima, A. and Ebihara, K. (2012). Degradation of pectin in the caecum
1071 contributes to bioavailability of iron in rats. *Brit. J. Nutr.* **107**: 1452-1457.
- 1072 Mladěnka, P., Macakova, K., Filipsky, T., Zatloukalova, L., Jahodar, L., Bovicelli, P.,
1073 Silvestri, I.P., Hrdina, R. and Saso, L. (2011). In vitro analysis of iron chelating activity
1074 of flavonoids. *J. Inorg. Biochem.* **105**: 693-701.
- 1075 Monnier L., Colette C. and Mirouze J. (1980). Evidence and mechanism for pectin-reduced
1076 intestinal inorganic iron absorption in idiopathic hemochromatosis. *Am. J. Clin. Nutr.*
1077 **33**: 1225-1232.
- 1078 Njoroge, D., Kinyanjui, P., Chigwedere, C., Christiaens, S., Makokha, A., Sila, D.,
1079 Hendrickx, M. (2016). Mechanistic insight into common bean pectic polysaccharide
1080 changes during storage, soaking and thermal treatment in relation to the hard-to-cook
1081 defect. *Food Res. Int.* **81**: 39-49.
- 1082 Nyman, M. and Asp, N.G. (1987). Effects of processing on dietary fiber in vegetables.
1083 *Lebensm. Wiss. Technol.* **20**: 29-36.
- 1084 Oatway, L., Vasanthan, T. and Helm, J.H. (2001). Phytic Acid. *Food Rev. Int.* **17**: 419-431.
- 1085 Oberleas D. and Chan H.C. (1997). Cation complexation by phytate. *Trace Elem. Electroly.*
1086 **14**: 173–176.
- 1087 Oghbaei, M. and Prakash, J. (2013). Effect of fractional milling of wheat on nutritional
1088 quality of milled fractions. *Trends Carbohydr Res.* **5**: 53-58.
- 1089 Ohta, A., Ohtsuki, M., Baba, S., Adachi, T., Sakata, T. and Sakaguchi, E. (1995). Calcium
1090 and magnesium absorption from the colon and rectum are increased in rats fed
1091 fructooligosaccharides. *J. Nutr.* **125**: 2417–2424.

- 1092 Olivares, A.B., Martinez, C., Lopez, G. and Ros, G. (2001). Influence of the design of a
1093 product on *in vitro* mineral availability of homogenized weaning foods. *Inno. Food Sci.*
1094 *Emer. Technol.* **2**: 181-197.
- 1095 Oliveira, A.P.D., Mateo, B.D.S.O., Fioroto, A.M., Oliveira, P.V.D. and Naozuka, J. (2018).
1096 Effect of cooking on the bioaccessibility of essential elements in different varieties of
1097 beans (*Phaseolus vulgaris* L.). *J. Food Compos. Anal.* **67**: 135-140.
- 1098 Osagie, A.U. and Eka, O.U. (1998). Antinutritional Factors. **In**: Nutritional Quality of Plant
1099 Foods, pp. 229-230. Osagie, A.U., Ed., Ambil Press Ltd, Nigeria.
- 1100 Osório-Díaz P., Bello-Pérez L.A., Sayago-Ayerdi S.G., Benítez-Reyes, M.D.P., Tovar, J. and
1101 Paredes-Lopes, O. (2003). Effect of processing and storage time on *in vitro* digestibility
1102 and resistant starch content of two bean (*Phaseolus vulgaris* L.) varieties. *J. Sci. Food*
1103 *Agr.* **83**: 1283-1288.
- 1104 Ozturk L., Yazici M.A., Yucel C., Torun A., Cekic C., Bagci A., Ozkan H., Braun H-J.,
1105 Sayers Z., Cakmak I. (2006). Concentration and localization of zinc during seed
1106 development and germination in wheat. *Physiol. Plant* **128**: 144-152.
- 1107 Pallares, A.P., Rousseau, S., Chigwedere, C.M., Kyomugasho, C., Hendrickx, M. and
1108 Grauwet, T. (2018). Temperature-pressure-time combinations for the generation of
1109 common bean microstructures with different starch susceptibilities to hydrolysis. *Food*
1110 *Res. Int.* **106**: 105-115.
- 1111 Pallares, A.P., Miranda, B.A., Truong A. N.Q., Kyomugasho, C., Chigwedere, C.M.,
1112 Hendrickx, M. and Grauwet, T. (2019). Process-induced cell wall permeability
1113 modulates the *in vitro* starch digestion kinetics of common bean cotyledon cells. *Food*
1114 *Res. Int.*
- 1115 Pandey, K.B. and Rizvi, S.I. (2009). Plant polyphenols as dietary antioxidants in human
1116 health and disease. *Oxid. Med. Cell Longev.* **2**: 270-278.
- 1117 Perron, N.R. and Brumaghim, J.L. (2009). A review of the antioxidant mechanisms of
1118 polyphenol compounds related to iron binding. *Cell Biochem. Biophys.* **53**: 75-100.
- 1119 Persson, H., Nair, B.M., Frolich, W., Nyman, M., Asp, N.G. (1987) Binding of mineral
1120 elements by some dietary fibre components—*In vitro* (II). *Food Chem.* **26**: 139-148.
- 1121 Persson, H. (1991). Binding of mineral elements by dietary fibre components in cereals—*In*
1122 *vitro* (III). *Food Chem.* **40**: 169–183.
- 1123 Petry, N., Egli, I., Zeder, C., Walczyk, T. and Hurrell, R. (2010). Polyphenols and phytic acid
1124 contribute to the low iron bioavailability from common beans in young women. *J. Nutr.*
1125 **140**: 1977–1982.
- 1126 Pizarro, F., Olivares, M., Valenzuela, C., Brito, A., Weinborn, V., Flores, S. and Arredondo,
1127 M. (2016). The effect of proteins from animal source foods on heme iron bioavailability
1128 in humans. *Food Chem.* **196**: 733-738.

- 1129 Platel, K. Eipeson, S.W. and Srinivasan, K. (2010). Bioaccessible Mineral Content of Malted
1130 Finger Millet (*Eleusine coracana*), Wheat (*Triticum aestivum*), and Barley (*Hordeum*
1131 *vulgare*). *J. Agric. Food Chem.* **58**: 8100–8103.
- 1132 Platel, K. and Srinivasan, K. (2016). Bioavailability of Micronutrients from Plant Foods: An
1133 Update. *Crit. Rev. Food Sci. Nutr.* **8398**: 1608–1619.
- 1134 Platt, S.R. and Clydesdale, F. M. (1987). Mineral binding characteristics of lignin, guar
1135 gum, cellulose, pectin, and neutral detergent fiber under simulated duodenal pH
1136 conditions. *J. Food Sci.* **52**: 1414-1419.
- 1137 Prochazkova, D., I. Bousova and N. Wilhelmova. (2011). Antioxidant and prooxidant
1138 properties of flavonoids. *Fitoterapia*, 82:513–523.
- 1139 Puna, R. and Paruchuri, U.R. (2004). Effect of maturity and processing on total, insoluble and
1140 soluble dietary fiber contents of Indian green leafy vegetables. *Int. J. Food Sci. Nutr.* **55**:
1141 561-567.
- 1142 Quideau, S. Deffieux, D., Douat-Casassus, D. and Pouységu, L. (2011). Plant polyphenols:
1143 Chemical properties, biological activities, and synthesis. *Angew. Chem. Int. Edit.* **50**:
1144 586–621.
- 1145 Raes, K., Knockaert, D., Struijs, K. and Van Camp, J. Role of processing on bioaccessibility
1146 of minerals: Influence of localization of minerals and antinutritional factors in the plant.
1147 *Food Sci. Technol.* **37**: 32-41.
- 1148 Reddy, M.B. and Love, M. (1999). Nutritional quality of vitamins and minerals. **In**: Impact
1149 of Processing on Food Safety, pp. 99-106. Jackson et al., Eds., Kluwer
1150 Academic/Plenum Publishers, New York.
- 1151 Rehman, Z. and Shah, W.H. (2004). Domestic processing effects on some insoluble dietary
1152 fibre components of various food legumes. *Food Chem.* **87**: 316-617.
- 1153 Rehman, Z. and Shah, W.H. (2005). Thermal heat processing effects on antinutrients, protein
1154 and starch digestibility of food legumes. *Food Chem.* **91**: 327-331.
- 1155 Rendleman, J.A. (1982). Cereal complexes: Binding of calcium by bran and components of
1156 bran. *Cereal Chem.* **59**: 302-309.
- 1157 Ribeiro, N.D., Maziero, S.M., Prigol, M., Nogueira, C.W., Rosa, D.P. and Possobom,
1158 M.T.D.F. (2012). Mineral concentrations in the embryo and seed coat of common bean
1159 cultivars. *J. Food Compos. Anal.* **1**: 89-95.
- 1160 Roberfroid, M.B. (2007). Inulin-type fructans: functional food ingredients. *J. Nutr.* **137**:
1161 2493-2502.
- 1162 Roohani, N., Hurrell, R., Kelishadi, R. and Schulin, R. (2013). Zinc and its importance for
1163 human health: An integrative review. *J. Res. Med. Sci.* **18**: 144-157.
- 1164 Ross, R.P., Morgan, S. and Hill, C. (2002). Preservation and fermentation: past, present and
1165 future. *Int. J. Food Microbiol.* **79**, 3-16.

- 1166 Rossander L., Sandberg A.S. and Sandström B. (1992). The influence of dietary fibre on
1167 mineral absorption and utilization. **In:** Dietary Fibre – A Component of Food, pp. 197-
1168 216. Schweizer, T.F. and Edwards, C.A., Eds., Springer Verlag, London.
- 1169 Ryan, P. and Hynes, M.J. (2007). The kinetics and mechanisms of the complex formation and
1170 antioxidant behaviour of the polyphenols EGCg and ECG with iron(III). *J. Inorg.*
1171 *Biochem.* **101**: 585–593.
- 1172 Saha, P. R., Weaver, C.M. and Mason, A.C. (1994). Mineral bioavailability in rats from
1173 intrinsically labeled whole wheat flour of various phytate levels. *J. Agr. Food Chem.* **42**:
1174 2531-2535.
- 1175 Saini, R.K., Nile, S.H. and Keum, Y.S. (2016). Food science and technology for management
1176 of iron deficiency in humans: A review. *Trends Food Sci. Tech.* **53**: 13–22.
- 1177 Sakai, K., Ohta, A., Shiga, K., Takasaki, M., Tokunaga, T. and Hara, H. (2000). The cecum
1178 and dietary short-chain fructooligosaccharides are involved in preventing
1179 postgastrectomy anemia rats. *J. Nutr.* **130**: 1608–1612.
- 1180 Sandberg, A. (2002). Bioavailability of minerals in legumes. *Brit. J. Nutr.* **88**: 281–285.
- 1181 Sandberg, A., Carlsson, N. and Svanberg, U. (1989). Effects of Inositol Tri-, Tetra-, Penta-,
1182 and Hexaphosphates on In Vitro Estimation of Iron Availability. *J. Food Sci.* **54**: 159–
1183 161.
- 1184 Sandström, B., Almgren, A., Kivistö, B. and Cederblad, Å. (1987). Zinc absorption in
1185 humans from meals based on rye, barley, oatmeal, triticale and whole wheat. *J. Nutr.*
1186 **117**: 1898-1902.
- 1187 Sandström, B. and Sandberg, A.S. (1992). Inhibitory effects of isolated inositol phosphates
1188 on zinc absorption in humans. *J. Trace Elem. Elect. H.* **6**: 99-103.
- 1189 Santos-Buelga, C. and Scalbert, A. (2000). Proanthocyanidins and tannin-like compounds -
1190 Nature, occurrence, dietary intake and effects on nutrition and health. *J. Sci. Food Agr.*
1191 **80**: 1094–1117.
- 1192 Scalbert, A., Morand, C., Manach, C. and Rémésy, C. (2002). Absorption and metabolism of
1193 polyphenols in the gut and impact on health. *Biomed. Pharmacother.* **56**: 279-282.
- 1194 Schlegel, P., Nys, Y. and Jondreville, C. (2010). Zinc availability and digestive zinc
1195 solubility in piglets and broilers fed diets varying in their phytate contents, phytase
1196 activity and supplemented zinc source. *Animal.* **4**: 200.
- 1197 Schlemmer, U., Frolich, W., Prieto, R.M. and Grases, F. (2009). Phytate in foods and
1198 significance for humans: food sources, intake, processing, bioavailability, protective role
1199 and analysis. *Mol. Nutr. Food Res.* **53**: 330-375.
- 1200 Schneeman, B. O. Ž. (1986). Dietary fibre: physical and chemical properties, methods of
1201 analysis, and physiological effects. *Food Technol.* **40**: 104-110.
- 1202 Schroeder, H.A. (1971) Losses of vitamin and trace minerals resulting from processing and
1203 preservation of foods. *Am. J. Clin. Nutr.* **24**: 562-566.

- 1204 Shahidi, F. (1997). Beneficial health effects and drawbacks of antinutrients and
1205 phytochemicals in foods. **In:** Antinutrients and phytochemicals in food, pp. 1-9.
1206 Shahidi, F., Ed, American Chemical Society, Washington.
- 1207 Shahidi, F., Chava, U.D., Naczk, M. and Amarowicz, R. (2001). Nutrient distribution and
1208 phenolic antioxidants in air-classified fractions of beach pea (*Lathyrus maritimus* L.). *J.*
1209 *Agric. Food Chem.* **49**: 926-933.
- 1210 Sila, D.N., Van Buggenhout, S., Duvetter, T., Fraeye, I., De Roeck, A., Van Loey, A. and
1211 Hendrickx, M. *Compr. Rev. Food Sci. F.* **8**: 86-104.
- 1212 Sitrin, M.D. (2014). Absorption of water-soluble vitamins and minerals. **In:** The
1213 gastrointestinal system, pp. 211-234. Leung, P.S., Ed., Springer, Netherlands.
- 1214 Sokrab, A.M., Ahmed, I.A.M. and Babiker, E.E. (2014). Effect of fermentation on
1215 antinutrients, and total and extractable minerals of high and low phytate corn genotypes.
1216 *J. Food Sci. Technol.* **51**: 2608-2615.
- 1217 Sreerama, Y.N., Neelam, D.A., Sashikala, V.B. and Pratapa, V. (2010). Distribution of
1218 nutrient and antinutrients in milled fractions of chickpea and horse gram: Seed coat
1219 phenolics and their distinct modes of enzyme inhibition. *J. Agric. Food Chem.* **58**: 4322-
1220 4330.
- 1221 Suliburska, J. and Krejpcio, Z. (2014). Evaluation of the content and bioaccessibility of iron,
1222 zinc, calcium and magnesium from groats, rice, leguminous grains and nuts. *J. Food Sci.*
1223 *Technol.* **51**: 589–594.
- 1224 Suma, P.F. and Urooj, A. (2014). Nutrients, antinutrients & bioaccessible mineral content (*in*
1225 *vitro*) of pearl millet as influenced by milling. *J. Food Sci. Technol.* **51**: 756-761.
- 1226 Svarc-Gajic, J. (2013). Antinutrients in Food. **In:** Nutritional Insights and Food Safety, pp. 1-
1227 37. Mandić, A., Sakač, M. and Mišan, A., Eds., Nova Science Publishers, Inc.
- 1228 Tahiri, M., Tressol, J.C., Arnaud, J., Bornet, F.R., Bouteloup-Demange, C., Feillet-Coudray,
1229 C., Brandolini, M., Ducros, V., Pépin, D., Brouns, F., Roussel, A.M., Rayssiguier, Y.
1230 and Coudray, C. (2003). Effect of short-chain fructooligosaccharides on intestinal
1231 calcium absorption and calcium status in postmenopausal women: A stable-isotope
1232 study. *Am. J. Clin. Nutr.* **77**: 449–457.
- 1233 Takeuchi K., Bjarnason I., Laftah A.H., Latunde-Dada G.O., Simpson R.J. and McKie A.T.
1234 Expression of iron absorption genes in mouse large intestine. *Scand. J. Gastroenterol.*
1235 **40**: 169-177.
- 1236 Tapiero, H. and Tew, K.D. (2003). Trace elements in human physiology and pathology: zinc
1237 and metallothioneins. *Biomed. Pharmacother.* **57**: 399-411.
- 1238 Thompson, S. A. and Weber C. W. (1979). Influence of pH on the binding of copper, zinc
1239 and iron in six fiber sources. *J. Food Sci.* **44**: 752-754.
- 1240 Tontisirin, K., Nantel, G. and Bhattacharjee, L. (2002). Food-based strategies to meet the
1241 challenges of micronutrient malnutrition in the developing world. *P. Nutr. Soc.* **61**: 243–
1242 250.

- 1243 Torre, M., Rodriguez, A.R. and Saura-Calixto, F. (1995). Interactions of Fe(II), Ca(II) and
1244 Fe(III) with high dietary fibre materials: A physicochemical approach. *Food Chem.* **54**:
1245 23–31.
- 1246 Towo, E., Matuschek, E. and Svanberg, U. (2006). Fermentation and enzyme treatment of
1247 tannin sorghum gruels: effects on phenolic compounds, phytate and in vitro accessible
1248 iron. *Food Chem.* **94**: 369-376.
- 1249 Troszynska, A., Bednarska, A., Latosz, A. and Kozłowska, H. (1997). Polyphenolic
1250 compounds in the seed coat of legume seeds. *Pol. J. Food Nutr. Sci.* **47**: 37-45.
- 1251 Van Buggenhout, S., Sila, D.N., Duvetter, T., Van Loey, A., Hendrickx, M. (2009). Pectins
1252 in processed fruits and vegetables: Part III-texture engineering. *Compr Rev Food Sci F*,
1253 8: 105-117.
- 1254 Van Den Heuvel, E.G., Muys, T., van Dokkum, W. and Schaafsma, G. (1999). Oligofructose
1255 stimulates calcium absorption in adolescents. *Am. J. Clin. Nutr.* **69**: 544–548.
- 1256 Van Soest, P.J. and Robertson, J.B. (1979). Systems of analysis for evaluating fibrous feeds.
1257 **In**: Standartization of Analytical Methodology for Feeds, pp. 49-60. Pigden, W.J., Balch,
1258 C.C. and Graham, M., Eds., IDRC, Ottawa CA.
- 1259 Viadel, B., Barberá, R. and Farré, R. (2006). Uptake and retention of calcium, iron, and zinc
1260 from raw legumes and the effect of cooking on lentils in Caco-2 cells. *Nutr. Res.* **26**:
1261 591–596.
- 1262 Vijayakumari, K. K., Siddhuraju, P., Pugalenth, M., & Janardhanan, K. K. (1998). Effect of
1263 soaking and heat processing on the levels of antinutrients and digestible proteins in seeds
1264 of *Vigna aconitifolia* and *Vigna sinensis*. *Food Chem.* **63**: 259–264.
- 1265 Vitali, D., Vedrina Dragojević, I. and Šebečić, B. (2008). Bioaccessibility of Ca, Mg, Mn and
1266 Cu from whole grain tea-biscuits: Impact of proteins, phytic acid and polyphenols. *Food*
1267 *Chem.* **110**: 62–68.
- 1268 Vohra, P., Gray, G.A. and Kratzer, F.H. (1965). Phytic Acid-Metal. *P. Soc. Exp. Biol. Med.*
1269 **5**: 8–10.
- 1270 Voragen, A.G.J., Coenen, G.J., Verhoef, R.P. and Schols, H.A. (2009). Pectin, a versatile
1271 polysaccharide present in plant cell walls. *Struct. Chem.* **20**: 263-275.
- 1272 Wang, L. and Sun., D.W. (2016). Heat and Mass Transfer in Thermal Food Processing. **In**:
1273 Thermal Food Processing: New Technologies and Quality Issues, Second Edition. Sun,
1274 D.W., Ed., CRC Press.
- 1275 Wang, N. (2005). Optimization of a laboratory dehulling process for lentil (*Lens culinaris*).
1276 *Cereal Chem.* **82**: 671-676.
- 1277 Wang, N., Hatcher, D.W., Tyler, R.T., Toews, R. and Gawalko, E.J. (2010). Effect of
1278 cooking on the composition of beans (*Phaseolus vulgaris* L.) and chickpeas (*Cicer*
1279 *arietinum* L.). *Food Res. Int.* **43**: 589-594.

- 1280 Wang, Y., Zeng, T., Wang, S.E., Wang, W., Wang, Q. and Yu, H.X. (2010). Fructo-
1281 oligosaccharides enhance the mineral absorption and counteract the adverse effects of
1282 phytic acid in mice. *Nutrition*, **26**: 305–311.
- 1283 Wapnir, R. (2000). Zinc deficiency, malnutrition and the gastrointestinal tract. *J. Nutr.* **130**:
1284 1388–1392.
- 1285 World Health Organization (2015). The Global Prevalence of Anaemia in 2011. WHO
1286 Report, 48.
- 1287 Xu, B. and Chang, S.K.C. (2008). Effect of soaking, boiling, and steaming on total phenolic
1288 content and antioxidant activities of cool season food legumes. *Food Chem.* **110**: 1-13.
- 1289 Xu, W., E. Han, and Z. Wang. (2019). Effect of tannic acid on corrosion behavior of carbon
1290 steel in NaCl solution. *Journal of Materials Science & Technology*, 1:64–75.
- 1291 Yap, K.W., Mohammed, S., Yazid, A.M., Maznah, I. and Meyer, D.M. (2005). Dose-
1292 response effects of inulin on the faecal short-chain fatty acids content and mineral
1293 absorption of formula-fed infants. *Nutr. Food Sci.* **35**: 208–219.
- 1294 Yoneda, S. and Nakatsubo, F. (1998). Effects of the hydroxylation patterns and degrees of
1295 polymerization of condensed tannins on their metal-chelating capacity. *J. Wood Chem.*
1296 *Technol.* **18**: 193–205.
- 1297 Younes, H., Demigné, C. and Rémésy, C. (1996). Acidic fermentation in the caecum
1298 increases absorption of calcium and magnesium in the large intestine of the rat. *Brit. J.*
1299 *Nutr.* **75**: 301–314.
- 1300 Zhou, J. R., Fordyce, E.J., Raboy, V., Dickinson, D. B., Wong, M. S., Burns, R. A. and
1301 Erdman Jr., J.W. (1992). Reduction of phytic acid in soybean products improves zinc
1302 bioavailability in rats. *J. Nutr.* **122**: 2466-2473.

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Table 1. Amounts of iron and zinc (mg) in plant-based foods (average per 100 mg) (Belitz, Grosch and Schieberle. 2009; Bielsalski 2013; Hayat et al. 2014; Saini, Nile and Keum 2016; Gregory et al. 2016).

	Vegetables	Fruits	Cereals	Legumes
Iron (mg 100 g⁻¹)	0.3-13.9	0.2-2.8	1.5-7.6	6.2-15.7
Zinc (mg 100 g⁻¹)	3.1-38.7	0.5	1.1-7.6	1.0-10.9

Figure 1. The egg-box model of calcium crosslinking in pectic polysaccharides. Reprinted, with permission, from Caffall and Mohnen (2009). The structure, function, and biosynthesis of plant cell wall pectic polysaccharides. *Carbohydrate research*, 14: 1879-1900. Copyright (2018).

1313

1314 **Figure 2.** Schematic representation of structural characteristics of pectin which can influence pectin-mineral binding capacity. For each characteristic: above, a possible
 1315 schematic presentation of a single pectin molecule is shown; below, a possible simplified scheme of pectin-mineral crosslinkings between pectin molecules is shown. This is a
 1316 simplified representation, combination between different characteristics is possible. GalA: Galacturonic acid residue; 6-O Me GalA: Galacturonic acid residues with
 1317 methylesterification at O-6 position; Gal: D-galactose; Rha: L- rhamnose; Ara: D- arabinose.

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1321 **Figure 3.** Basic chemical structure of phytic acid. Reprinted, with permission, from Kumar et al. (2010). Dietary

1322 roles of phytate and phytase in human nutrition: A review. Food Chemistry, 120: 945–959. Copyright (2018).

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1328

1329 **Figure 5.** Chemical structure of tannic acid. Reprinted, with permission, from Xu, Han and Wang (2019). Effect
 1330 of tannic acid on corrosion behavior of carbon steel in NaCl solution. *Journal of Materials Science & Technology*,
 1331 1:64–75. Copyright (2018).

Figure 6. Expected octahedral coordination geometry of general iron-polyphenol complexes. Gallols, R=OH; catechols, R=H. Reprinted, with permission, from Perron and Brumaghim (2009). A review of the antioxidant mechanisms of polyphenol compounds related to iron binding. *Cell Biochemistry and Biophysics*, 53: 75-100.

Figure 7. Fenton and Haber-Weiss reactions.

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Figure 8. Schematic representation of possible plant tissue disintegration after mechanical disruption. During mechanical disruption two characteristic tissue failure modes may occur: cell separation and/or cell breakage. In the case of cell breakage, the cell wall is ruptured and cell content (e.g. starch, protein and minerals) is released.