

# Nutritional Quality of Fruits and Vegetables

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## I. Introduction

Horticultural crops are some of the main components of a healthy diet. The constituents obtained by the human body from fruits and vegetables include water, carbohydrates, fats, proteins, fiber, minerals, organic acids, pigments, vitamins and antioxidants, among others. Fruits and vegetables, especially, are a good source of fiber, selected minerals, vitamins and antioxidants. Most fruits and vegetables are available almost year-round in a wide variety and they not only taste good, but they also have favorable attributes of texture, color, flavor and ease of use. They can be fresh, cooked, hot or cold, canned, pickled, frozen or dried.

Fruits and vegetables are consumed at all times, and due to their convenient size; they are an excellent between-meal snack. They are relatively low in calories and fat (avocado and olives being the exceptions), they have no cholesterol, they are rich in carbohydrates and fiber, they contain vitamin C and carotene, and some are a good source of vitamin B<sub>6</sub>. Fruits and vegetables are relatively low in sodium and high in potassium. Ascorbic acid in fruits and vegetables enhances the bioavailability of iron in the diet. Because of all these characteristics, fruits and vegetables have a unique role in a healthy diet. A growing body of research has shown that fruit and vegetable consumption is associated with reduced risk of major diseases, and possibly delayed onset of age-related disorders, promoting good health. However, in many cases fruit and vegetable consumption is still below the dietary guideline goal of consuming 5–10 servings each day. The nutritional value of fruits and vegetables depends on their composition, which shows a wide range of variation depending on the species, cultivar and maturity stage. The composition of fruits and vegetables includes a great number of metabolites however, it could be predicted that no single commodity might be rich in all these constituents. This chapter describes the general characteristics of the components of fruits and vegetables, related to their benefits as food sources.

## II. Traditional components

### A. Water

The most abundant single component of fruits and vegetables is water, which may account for up to 90% of the total mass. The maximum water content varies between individual fruits and vegetables, because of structural differences. Cultivation conditions that influence structural differentiation may also have a marked affect.

### B. Organic acids

There are two types of acids, namely aliphatic (straight chain) and aromatic acids. The most abundant acids in fruits and vegetables are citric and malic (both aliphatic) acids. However, large amounts of tartaric acid occur in grapes. Malic acid is the major component in oranges and apples. The acid content of fruits and vegetables generally decreases during maturation. For example, the citric acid content of clingstone peaches

decreases faster than the malic acid content, while the malic acid content of apples and pears decreases faster than the citric acid content. Aromatic organic acids occur in several fruits and vegetables, but in very low concentrations. Benzoic acid occurs in cranberries, quinic acid in bananas and chlorogenic acid in potatoes. Organic acids play an important role in the sugar to acid ratio, which affects the flavor of fruits and vegetables. The distribution of acids within a fruit is not uniform.

### C. Proteins

Proteins represent less than 1% of the fresh mass of fruit and vegetable tissues. Leguminous seeds are rich in protein, containing 15% to 30%. The proteins of fruits and vegetables are built from amino acids, but other related simple nitrogenous compounds also occur. Fruits, vegetables and legumes account for 1.2%, 5.5% and 6.1%, respectively, of the protein in the US food supply (Hiza and Bente, 2007). Fruits are low in proteins, but tree nuts are a good source of high-quality proteins. The protein content of fresh fruits or vegetables is calculated by multiplying the total nitrogen content by a factor of 6.25. This calculation uses the fact that protein is comprised of about 16% nitrogen, and the assumption that all nitrogen present is protein. The conversion ignores the fact that appreciable amounts of simple nitrogenous substances can be present in an uncombined form. In potatoes, 50% to 60% of the nitrogen occurs in the form of simple soluble constituents, while in apples the estimates range from 10% to 70% (Salunkhe et al., 1991). Senescent tissues, such as those of overripe fruits, usually contain especially high proportions of non-protein nitrogen. Asparagine is abundant in potatoes and apples as non-protein nitrogen fractions. Pears and oranges are rich in proline, and black and red currants in alanine.

### D. Lipids and fatty acids

Plant lipids represent a very broad group of compounds with functions that vary among products. Lipids are an energy source for plants during germination, forming components of cellular membranes and cuticular waxes, and they are mainly present as triglycerides (esters of glycerol and three fatty acids) or phospholipids (in which one fatty acid has been replaced by a phosphate group). Generally, most postharvest products are relatively low in total lipids, except for avocados, olives and many seeds. The fat content of fruits and vegetables is usually below 1% and varies with the product. Examples of fat content on a dry mass basis are:

- avocado: 35–70%;
- olive: 30–70%;
- grape: 0.2%;
- banana: 0.1%; and
- apple: 0.06%.

Many of the physical and chemical properties of lipids are due to the fatty acids present in their structure. Fatty acids are aliphatic monocarboxylic acids that may be saturated or unsaturated to varying degrees. Saturated fatty acids do not contain any double bonds along the chain. Monounsaturated fatty acids have a single double

bond in the hydrocarbon chain, and polyunsaturated fatty acids have more than one double bond. Fatty acids in plants usually range from 4- to 26-carbons in size, but oleic acid (18:1) and linoleic acid (18:2) are the most prevalent in nature. Olive oil and other fats high in monounsaturated fatty acids are becoming well-known for helping to lower LDL-cholesterol (the so-called “bad” cholesterol), while protecting HDL-cholesterol (“good” cholesterol) when consumed in moderation in place of saturated fats. The difference among oils is not in their caloric content, but in their composition. Fats derived from animal sources (e.g. butter, cream, hard cheeses) have a high proportion of saturated fats, while oils from plant sources, such as olive and canola, have the lowest (Table 5.1).

Fatty acids are necessary for human bodily functions, where they are used primarily to produce hormone-like substances that regulate a wide range of functions including blood pressure, blood clotting, blood lipid levels, the immune response and the inflammatory response. The human body can produce most fatty acids, except for linoleic acid and  $\alpha$ -linolenic acid, which are widely distributed in plant oils. These essential fatty acids are polyunsaturated fatty acid members of the omega-6 and omega-3 fatty acid series.

Each double bond, depending on its geometry, can be in either a *cis* or a *trans* conformation. In *cis* bonds, the two carbons next to the unsaturated site bond atoms are oriented to the same side. Therefore, in restricted environments, such as when fatty acids are part of a phospholipid in a lipid bilayer or triglycerides in lipid droplets, *cis* bonds limit the ability of fatty acids to be closely packed and therefore, could affect the melting temperature of the membrane or the fat. A *trans* configuration, by contrast, means that the two carbons next to the double bond are oriented to opposite sides. As a result, they do not cause the chain to bend much, and their shape is

**Table 5.1** Fatty acid, vitamin E and cholesterol composition of some common dietary fats

	Saturated (%)	Monounsaturated (%)	Polyunsaturated (%)	Cholesterol (mg 100 g <sup>-1</sup> )
<b>Animal fats</b>				
Lard	40.8	43.8	9.6	93
Butter	54.0	19.8	2.6	230
<b>Vegetable fats</b>				
Coconut oil	85.2	6.6	1.7	0
Palm oil	45.3	41.6	8.3	0
Cottonseed oil	25.5	21.3	48.1	0
Wheat germ oil	18.8	15.9	60.7	0
Soya oil	14.5	23.2	56.5	0
Olive oil	14.0	69.7	11.2	0
Corn oil	12.7	24.7	57.8	0
Sunflower oil	11.9	20.2	63.0	0
Safflower oil	10.2	12.6	72.1	0
Canola oil	5.3	64.3	24.8	0

Source: Kays, S.J. 1997.

similar to straight saturated fatty acids. In plant sources, unsaturated fatty acids naturally occur in the *cis* form. *Trans* fatty acids might be present in some fats of animal origin, or might be the result of oil processing (e.g. hydrogenation of vegetable oils). The differences in geometry between the various types of unsaturated fatty acids, as well as between saturated and unsaturated fatty acids, play an important role in biological processes and in the construction of biological structures (such as cell membranes). Medical research suggests that amounts of *trans* fats correlate with circulatory diseases, such as atherosclerosis and coronary heart disease, more than the same amount of non-*trans* fats, for reasons that are not yet completely understood.

### E. Metabolizable carbohydrates

After water, carbohydrates are the most abundant constituents in fruits and vegetables, representing 50% to 80% of the total dry weight. Carbohydrate functions include, among others, the storage of energy reserves and the make-up of much of the structural framework of cells. Simple carbohydrates, which are also the immediate products of photosynthesis, are important components of sensorial quality attributes. Carbohydrates, like proteins, yield  $4 \text{ kcal g}^{-1}$ , while fats yield  $9 \text{ kcal g}^{-1}$ . In many products, monosaccharides comprise a major portion of the total sugars. Glucose and fructose are the predominant forms of simple sugars found, especially, in fruits. Sucrose, the primary transport form of carbohydrate in most plants, is a disaccharide yielding glucose and fructose upon hydrolysis. Glucose, fructose and sucrose are water-soluble and together they comprise most of the sugars associated with the sweet taste of fruits and vegetables. The relative proportions of glucose and fructose vary from fruit to fruit and, to a lower extent, in the same fruit according to maturity. In many fruits (e.g. apple, pear, strawberry, grape) glucose and fructose are present in greater amounts than sucrose, but in certain vegetables, such as parsnip, beetroot, carrot, onion, sweet corn, pea and sweet potato, and in some ripe fruits such as banana, pineapple, peach and melon, the sucrose content is higher. Traces of other mono- and disaccharide sugars such as xylose, arabinose, mannose, galactose and maltose may also be present in small amounts (Salunkhe et al., 1991). Some fruits of the *Rosaceae* family could also have significant levels of the sugar alcohol sorbitol. Total carbohydrate content also includes starches, which are organized into small grains, either within the chloroplasts or in some cases in specialized plastids (amyloplasts). Some non-starchy root vegetables, such as parsnip, beetroot and carrot, are relatively rich in simple sugars, containing between 8% and 18% of total carbohydrates. However, most vegetables contain smaller amounts of metabolizable carbohydrates.

### F. Dietary fiber

#### Definition and composition

Several definitions of fiber, either physiological or based on the measurement techniques used for its determination, have been put forward (Slavin, 2005). An expert panel adopted the term “dietary fiber consisting of non-digestible carbohydrates and lignin that are intrinsic and intact in plants” (Institute of Medicine, 2001).

Dietary fiber includes very diverse macromolecules exhibiting a large variety of physico-chemical properties. The main components included as fiber are cellulose, hemicelluloses, pectins, lignin, resistant starch and non-digestible oligosaccharides.

**Cellulose** is a cell wall polymer of  $\beta$ -1,4-linked glucose (Brett and Waldron, 1996). Within the cell wall, the glucan chains are associated with hydrogen bonds to form assemblages highly resistant to degradation, known as microfibrils (Carpita and McCann, 2000). In fruits and vegetables, the cell wall constitutes 1% to 2% of the fresh weight, and cellulose could be as much as 33% of that amount. In general, with the exception of avocado in which the whole cell wall seems to be degraded (O'Donoghue et al., 1994), little change in cellulose content occurs during ripening (Brummell, 2006).

**Hemicelluloses** Several cell wall polymers soluble in alkalis are classified as hemicelluloses or cross-linking glycans (Brummell and Harpster, 2001). Within the primary cell wall, hemicellulose levels are usually around 30% (Carpita and McCann, 2000). The most common hemicellulose polymer in dicotyledonous species is known as xyloglucan, composed as cellulose of a backbone of  $\beta$ -1,4-linked glucose, but with lateral chains of the pentose xylose ( $\alpha$ -1,6 linked). These xylosyl residues can be modified further, with galactose, arabinose and/or fucose (Brummell, 2006). Xylans are hemicellulosic compounds more abundant in monocotyledonous species, having a backbone of  $\beta$ -1,4-linked xylose which could be decorated with side chains of arabinose and/or glucuronic acid. Other hemicellulosic compounds usually less abundant include glucomannans, galactomannans and galactoglucomannans (Carpita and McCann, 2000).

**Pectins** Fruit tissues are particularly rich in pectins, which can account for up to 40% of the total cell wall polysaccharides. Pectins are also a diverse group of polymers rich in galacturonic acid (Ridley et al., 2001). The most abundant pectic polysaccharide in the cell wall is homogalacturonan, a homopolymer of  $\alpha$ -1,4-linked galacturonic acid residues, with variable degrees of methyl esterification at C6 (Willats et al., 2001). The degree of polymerization and the proportion of methyl esters affect the solubility of pectins. Pectins are deposited in the cell walls, with a high degree of esterification, and methyl ester usually decreases during ripening. Another modification commonly observed in several fruits during ripening is a reduction in pectin polymer size (Brummell, 2006; Vicente et al., 2007b). The extent of pectin depolymerization is variable, ranging from fruits such as avocado showing a dramatic downshift in polyuronide size (Huber and O'Donoghue, 1993) to products in which these changes are negligible, such as pepper or some berries (Brummell, 2006; Vicente et al., 2007a). Rhamnogalacturonan I (RG I) and rhamnogalacturonan II (RG II) are pectic polysaccharides which are also present in the plant cell wall. RG I has a backbone of alternating  $\alpha$ -1,2-rhamnosyl and  $\alpha$ -1,4-galacturonosyl residues (Willats et al., 2001), with side chains rich in arabinose and galactose (Carpita and McCann, 2000). Losses in the side chains are a common feature in fruit ripening, which can also affect pectin solubility and hydration potential (Gross and Sams, 1984; Redgwell et al., 1997). RG II is the most complex polysaccharide present in the cell wall; it has the ability to form dimers via borate diester bonds (O'Neill et al., 2004; Kobayashi et al., 1996). Pectins, which are used in the commercial manufacture

of jams and jellies, are extracted from certain fruits and vegetables such as citrus, apples and beets.

**Lignin** is one of the most abundant biopolymers in nature (Boerjan et al., 2003). It is an aromatic heteropolymer formed by the association of three hydroxycinnamyl alcohol derivatives (p-coumaryl, coniferyl and sinapyl alcohols) (Reddy et al., 2005). Lignin is a highly resistant polymer present in secondary cell walls, and is associated with fibers and xylem vessels. In the case of fruits and vegetables, lignin content is relatively low.

**Resistant starch** Starches are polysaccharides, composed of a number of glucose molecules linked together with  $\alpha$ -D-(1-4) and/or  $\alpha$ -D-(1-6) linkages (Sajilata et al., 2006). Resistant starch consists of starch and its degradation products that are not digested in the small intestine (Asp, 1994). Legumes are rich in resistant starch, and as much as 35% of their starch could escape digestion (Marlett and Longacre, 1996). Green bananas and potato are also relatively rich in resistant starch. Very little information is available about the resistant starch content of foods and the amount of resistant starch in a typical diet.

**Non-digestible oligosaccharides (NDOs)** Oligosaccharides are low molecular weight carbohydrates intermediate in nature between simple sugars and polysaccharides (Mussatto and Mancilha, 2007). While several oligosaccharides might be hydrolyzed in the digestive tract, others might resist the digestive process. Some of them include raffinose (trisaccharide composed of galactose, fructose, and glucose), stachyose (two galactose, one glucose and one fructose unit, linked sequentially) and verbascose (three galactose, one glucose and one fructose unit, linked sequentially). Legumes are rich in NDOs (Mussatto and Mancilha, 2007).

### **Benefits of fiber intake**

One of the most well known benefits of dietary fiber is the modulation of function of the intestinal tract (Institute of Medicine, 2001). Meals rich in fiber promote satiety earlier, and are usually relatively low in calories compared to meals rich in other food types (Marlett et al., 2002). Several works have also associated diets rich in dietary fiber with positive effects in disease prevention (see Institute of Medicine, 2001). Some works have established an inverse association between fiber intake and coronary disease (Rimm et al., 1996; Wolk et al., 1999). Total fruit and vegetable consumption was inversely associated with colorectal cancer risk (Terry et al., 2001). Current national dietary guidelines recommend an increased dietary fiber intake and suggest that fiber, independent of fat intake, is an important dietary component for the prevention of some diseases. Recommendations for adult dietary fiber intake generally fall in the range of 20 to 35 grams per day. The average fiber intake of adults in the US is less than half of this recommended level (Marlett and Slavin, 1997).

### **Sources of fiber**

Whole grains (especially the pericarp) and also fruits and vegetables are considered very good sources of fiber (Anderson et al., 2007). In 2004, the primary contributors of fiber to the food supply were fruits and vegetables (37.1%), followed by grain products (36.0%) and legumes (13.3%) (Hiza and Bente, 2007). Fiber content of

**Table 5.2** Fiber content in selected fruits, vegetables and nuts

Product	Dietary fiber (%)
Almond	12.2
Apple	2.4
Asparagus	2.1
Avocado	6.8
Banana	2.6
Broccoli	2.6
Carrot	2.8
Kiwifruit	3.4
Lettuce	2.1
Onion	1.7
Orange	2.4
Pea	2.6
Peach	1.5
Peanut	8.5
Pear	3.1
Pepper	2.1
Pineapple	1.4
Plum	1.4
Potato	2.2
Prunes	7.1
Raisin	3.7
Spinach	2.2
Strawberry	2.0
Tomato	1.2
Walnut	6.7

Source: US Department of Agriculture, 2008.

fruits and vegetables is usually in the range of 1% to 3% (Table 5.2). Nuts, legumes and dried fruits have higher levels of fiber than fruits and vegetables. The nature of fiber varies among food sources. For instance, pectin is low in grains, but constitutes approximately 20% to 35% of the fiber in fruits, vegetables, legumes and nuts. Hemicelluloses account for about half of the total fiber in grains, and approximately 25% to 35% of the total fiber in other foods. Cellulose is one third or less of the total fiber in most foods (Marlett, 1992). Besides total fiber content, some relevant properties include particle size and bulk volume, surface area characteristics, hydration and rheological properties, and adsorption or entrapment of minerals and organic molecules (Guillon and Champ, 2000). The main modifications during storage of most fruits and vegetables occur because of changes in the solubility and molecular size of the cell wall constituents due to the action of several proteins (Brummell, 2006; Fisher and Bennett, 1991). In some products, modification in fiber fractions could negatively affect quality. For instance, asparagus shows rapid hardening of the basal portions of the spears during storage related to modifications of fiber, such as



increased deposition of lignin (Saltveit, 1988). In general, preparation of fruits and vegetables by typical home methods or commercial processing does not seem to cause great loss of fiber (Zyren et al., 1983).

## G. Vitamins

Vitamins are organic molecules required in trace amounts for normal development, which cannot be synthesized in sufficient quantity by the organism and must be obtained from the diet. The term “vitamin” derives from the words “vital amine” because the first vitamin discovered (thiamine) contained an amino group. The 14 vitamins known today are vitamin A (retinol), B complex [B1 (thiamine), B2 (riboflavin), B3 (niacin), B5 (pantothenic acid), B6 (pyridoxine), B9 (folate/folic acid), biotin, choline and B12 (cyanocobalamin)] and vitamins C, D, E and K. They do not have common functions or structure and are usually grouped into fat-soluble (A, D, E and K) and water-soluble (B group and C) molecules. The vitamins present in fruits and vegetables make an important contribution to human nutrition, as they have specific functions in normal body performance. The vitamin content of fruits and vegetables shows a wide variation among species (Salunkhe et al., 1991). Differences within cultivars occur, as well as between different batches of the same cultivar grown under different environmental and orchard conditions (Rodriguez-Amaya, 2001; Lee and Kader, 2000).

### Vitamin A

Carotenoids are liposoluble pigments responsible for the yellow, orange and red color of several fruits and vegetables. Carotenoids are terpenoids formed by eight isoprene units (2-methyl-1,3-butadiene) and derived from isopentenyl diphosphate. Those having an unsubstituted  $\beta$ -ring with an 11-carbon polyene chain have provitamin A activity (Meléndez-Martínez et al., 2007), such as  $\alpha$ -carotene,  $\beta$ -carotene and cryptoxanthin (Kopsell and Kopsell, 2006). The structural requirement for vitamin A is satisfied by around 60 carotenoids (Rodriguez-Amaya, 2001). Vitamin A plays an important role in vision, cell division and differentiation, bone development and reproduction. The average daily requirement for vitamin A for an adult is estimated at 5000 international units (1 IU = 0.3  $\mu$ g retinol or 0.6  $\mu$ g  $\beta$ -carotene).

Among this group there are, basically, two different classes: carotenes containing C and H (e.g.  $\alpha$ -carotene,  $\beta$ -carotene, lycopene, etc.), and oxygenated derivatives known as xanthophylls, such as lutein, violaxanthin and zeaxanthin. Carotenoids in plants have functions related to radiation interception, mainly in the blue–green region of the spectrum, which may be transferred to the photosynthetic centers (Kopsell and Kopsell, 2006). Moreover, these pigments protect the photosynthetic structures from excessive energy (Grusak and Della Penna, 1999). They are usually present in low concentrations and their levels are highly variable among species. Fruits and vegetables account for only 30% of the vitamin A in the American diet (Hiza and Bente, 2007). Vegetables that can supply useful amounts of carotene include carrots, pumpkins and squashes.

Compared to vegetables, fruits are generally not as good a source of carotenoids, although there are a few notable exceptions such as apricot, mango, citrus, papaya

**Table 5.3** Carotene content (mean values) of selected fruits

Product	Carotene ( $\mu\text{g } 100\text{g}^{-1}$ )
Mango	1800
Cantaloupe	1000
Pawpaw	810
Guava	435
Apricot	405
Plum	295
Watermelon	230

Source: Rodríguez-Amaya, 2001.

and watermelon (Table 5.3). Tomatoes and peppers also contain high levels of carotenoids. Their distribution is not usually uniform and in general, their accumulation is higher in the peel than in the pulp (Rodríguez-Amaya, 2001). To date, over 600 different carotenoids have been identified, but only a few of them are commonly found in produce.  $\beta$ -carotene, the most widely studied carotenoid, accumulates in carrots; lycopene is common in tomato and watermelon. Other pigments within this group include  $\alpha$ -carotene,  $\beta$ -carotene, lutein, cryptoxanthin and zeaxanthin. In tomatoes, peaches and carrots the synthesis of carotene can continue after harvest. There is no difference between the carotene content of cooked vegetables and that of raw vegetables. Absorption of carotene can only be effective if the diet includes a minimum of 15% fat. The manner in which the food is prepared also determines the amount of carotene that will be absorbed. Homogenized carrots allow for the best absorption, followed by shredded carrots and whole carrots.

### Vitamin B complex

Thiamine is required in the human body for the metabolism of carbohydrates. A daily intake of 1–2 mg is generally considered as necessary for a normal adult. Legumes are especially rich in thiamine. Compared with ascorbic acid, thiamine is relatively stable at cooking temperatures, especially in a slightly acidic solution. However, losses of 25% to 40% may occur during cooking.

The average human requirement for riboflavin is estimated to be 1–2 mg per day. Green vegetables such as beans, beets, peppers and spinach are particularly rich in riboflavin. Starchy vegetables and fruits are relatively poor sources of riboflavin. Niacin, also known as nicotinic acid, is a precursor to NADH, NAD,  $\text{NAD}^+$  and NADP, which play essential roles in living organisms. A daily intake of 10 mg to 15 mg niacin is recommended. There is evidence that niacin can be synthesized in the body from tryptophan. Almonds are a rich source, but no fruits or vegetables can be singled out as being rich in niacin except perhaps, cape gooseberry and avocado. Niacin is relatively stable.

Vitamin B<sub>6</sub> (pyridoxal phosphate) is a cofactor in many transamination, decarboxylation and deamination reactions (e.g. in plants, formation of ACC by ACC synthase requires pyridoxal phosphate as a cofactor) (Ramalingam et al., 1985). Common

symptoms of vitamin B<sub>6</sub> deficiency include dermatitis around the eyes, elbows and mouth, along with soreness of the mouth and a red tongue. It can also lead to dizziness, vomiting, weight loss and severe nervous disturbances (Salunkhe et al., 1991). Vitamin B<sub>6</sub> is present in appreciable amounts in beans, cabbage, cauliflower, spinach, sweet potatoes, grapes, prunes, avocados and bananas. It is fairly heat stable.

Pantothenic acid can be obtained from fresh, canned or frozen fruits and vegetables containing this vitamin if they are included in the diet. Pantothenic acid occurs widely in peas, beans, nuts, broccoli, mushrooms, potatoes and sweet potatoes. Symptoms of pantothenic acid deficiency in the diet include fatigue, headaches, sleep disturbance, tingling of hands and feet and lack of antibody production.

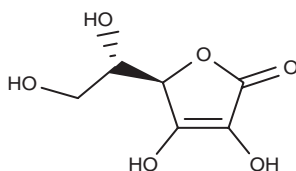
Biotin is stable during cooking, processing and storage of fresh, canned and frozen fruits and vegetables. Deficiency leads to depression, sleeplessness and muscle pains. It is synthesized in the intestinal tract (Salunkhe et al., 1991).

Folic acid is essential for reproduction and normal growth. The vitamin is present in fruits, spinach, cabbage and other green vegetables. Lack of folic acid in the diet can cause a red tongue, diarrhea and anemia. Choline is heat-stable and occurs in dried legumes and vegetables. Choline deficiency in humans has never been reported.

Vitamin B<sub>12</sub> does not occur in fruits and vegetables. Because vitamins of the B group are water-soluble, leaching losses occur during cooking.

### Vitamin C

Ascorbic acid (AsA) and its first oxidation product dehydroascorbic acid (which can be reduced in the human body) might be considered as vitamin C. AsA is a water-soluble carbohydrate-derived compound showing antioxidant and acidic properties due to the presence of a 2,3-enediol moiety (Figure 5.1). Humans and a few other species are not able to synthesize AsA (Chatterjee, 1973), because the gene coding for the last enzyme in the pathway (L-gulonono-1,4-lactone oxidase) is non-functional (Valpuesta and Botella, 2004). Plants synthesize AsA via a pathway that uses L-galactose as a precursor (Smirnoff and Wheeler, 2000; Smirnoff, 2000). Another pathway using galacturonic acid, which might be recycled from cell wall pectin degradation, has been suggested in plants (Agius et al., 2003). AsA has crucial biological functions in humans, such as its participation in collagen biosynthesis (Murad et al., 1981). Even though nutritional deficiencies are rare in modern western cultures, it is generally recognized that dietary AsA also has important health benefits for the consumer, and an increased intake of vitamin C has been associated with a reduced incidence of some diseases and disorders (Carr and Frei, 1999; Hancock



**Figure 5.1** Structure of ascorbic acid, a main antioxidant present in fruits and vegetables.

and Viola, 2005). Furthermore, in meat-poor diets, dietary AsA can contribute to the improved uptake of iron (Frossard et al., 2000). The recommended dietary allowance of vitamin C for men is 75 mg daily, while the recommended dietary allowance for young women is higher, at 90 mg daily (Levine et al., 2001).

Fruits, vegetables and juices are the main dietary sources of vitamin C. Fruits and vegetables account for 90% of the vitamin C in the US food supply (Hiza and Bente, 2007). Its concentration depends on the product considered (Noctor and Foyer, 1998), ranging from 1 to 150 mg 100 g<sup>-1</sup> fresh weight (FW) (Lee and Kader, 2000). Vitamin C is present in fresh fruits and vegetables, as well as in fruit juices. Fruits, particularly tropical species, and leafy vegetables are rich in ascorbic acid. Rosehip, jujube and guava have very high levels of ascorbic acid. Other good sources of AsA include persimmon, strawberry, kiwifruit, peppers, and citrus fruit, and spinach, broccoli and cabbage among vegetables (Table 5.4).

Wide variations in vitamin C content also exist within cultivars. For instance, AsA content in *Actinidia deliciosa* fruit varies from 29 to 80 mg 100 g<sup>-1</sup> FW, depending on the cultivar (Nishiyama et al., 2004). Even more dramatic variations were found in berry fruits, with levels of AsA ranging from 14 to 103 mg 100 g<sup>-1</sup> FW among cultivars of raspberry, blackberry, red currant, gooseberry and cornelian cherry (Pantelidis et al., 2007). For any given product, the levels of AsA are highly variable, depending on genetic and environmental factors (reviewed in Lee and Kader, 2000). A main environmental factor determining the level of ascorbic acid is radiation interception. In general, the greater the amount of sunlight received during growth, the higher the ascorbic acid content. The retention of AsA is also markedly affected by storage and processing. Potatoes lose up to 75% to 80% of the original levels over nine months of storage. In most cases, other fruit and vegetable AsA levels decline during storage, because the losses are accelerated by storage at high temperatures. Bruising and mechanical damage greatly increase the rate of ascorbic acid loss. Ascorbic acid is highly susceptible to oxidation, either directly or through the enzyme ascorbate oxidase catalyzing the oxidation of AsA to dehydroascorbic acid, with the concomitant reduction of molecular oxygen to water (Sanmartin et al., 2007). Ascorbic acid can even be oxidized during eating, while food is being chewed. However, it is important to consider that the first breakdown product of AsA,

**Table 5.4** Vitamin C content (mean values) of selected fruits

Product	Vitamin C (mg 100 g <sup>-1</sup> fresh weight)
Guava, raw	184
Kiwi, raw	118
Litchi, raw	72
Pawpaw, raw	62
Strawberry, raw	57
Citrus fruits	31–53
Cantaloupe	42

Source: Salunkhe et al., 1991.

dehydroascorbic acid, still has vitamin C activity and all activity is lost if oxidation proceeds beyond this stage (Salunkhe et al., 1991). When vegetables are cooked before eating, high losses of vitamin C can occur. For instance, starchy vegetables may lose between 40% and 80% of their vitamin C during cooking, because of leaching and oxidation. Loss of vitamin C can be reduced by steaming or by placing the vegetables directly into boiling water. Freezing reduces vitamin C slightly, but at the end of long-term frozen storage (12 months), a significant decrease (33% to 55%) in vitamin C can occur (de Ancos et al., 2000).

### Vitamin E

Vitamin E includes tocopherols and tocotrienols. They can be in eight different forms (four tocopherols and four tocotrienols). All the isomers have aromatic rings with a hydroxyl group that can donate hydrogen atoms to reduce reactive oxygen species (ROS). The different isomers are named alpha ( $\alpha$ ), beta ( $\beta$ ), gamma ( $\gamma$ ) and delta ( $\delta$ ), and this is related to the number and position of methyl groups in the ring. Each of the forms has its own vitamin E activity,  $\alpha$ -tocopherol being the most active (see Figure 5.2). Vitamin E deficiency results in stunted growth. In general, vitamin E levels are more abundant in oily seeds, olives, nuts, peanuts, avocados and almonds. Even though the levels of tocopherol in broccoli and leafy vegetables are lower than in fat-rich products, they are good sources compared to other fruits and vegetables. Vitamin E is highly susceptible to oxidation during storage and processing.

### Vitamins D and K

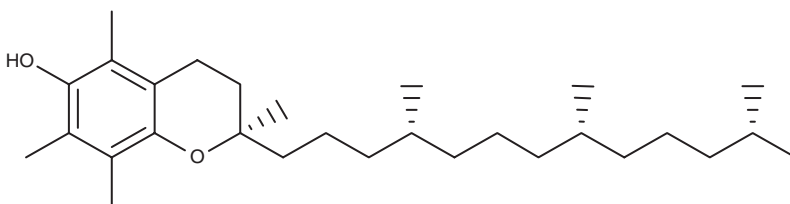
Vitamin D is a group of fat-soluble compounds. The main forms of vitamin D are ergocalciferol and cholecalciferol. It occurs only in trace amounts in fruits and vegetables.

Vitamin K is essential for blood coagulation, but dietary deficiency is uncommon. The recommended daily intake is 120  $\mu$ g. It occurs abundantly in lettuce, spinach, cauliflower and cabbage. As well as direct intake, it can also be produced by bacteria in the intestines.

## III. Antioxidants in fruits and vegetables

### A. Oxidative damage and antioxidants

Imbalance in the production of reactive oxygen species (ROS) leading to negative cellular alterations is known as oxidative damage, which is caused by several molecules

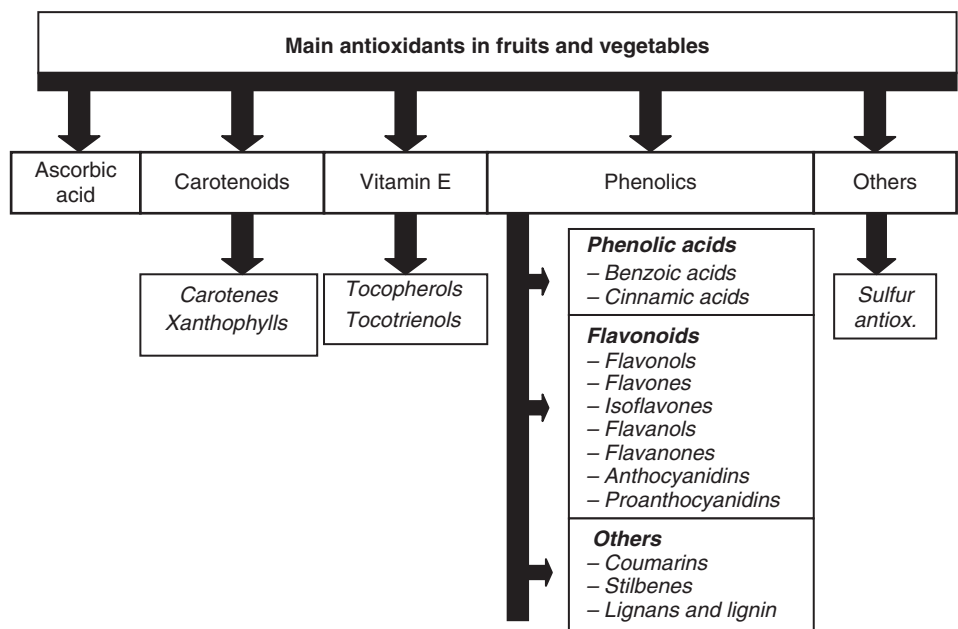


**Figure 5.2** Structure of tocopherol.

(Mittler, 2002). Reactive oxygen species are partially reduced forms of oxygen such as singlet oxygen, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), superoxide (O<sub>2</sub><sup>-•</sup>) or hydroxyl radical (OH<sup>-•</sup>) (Asada, 1999). Some, but not all of the components able to cause oxidative damage are free radicals (i.e. molecules with unpaired electrons, which determine their high reactivity). Currently, there is overwhelming evidence showing that the ROS can alter proteins, lipids and nucleic acids, causing deleterious modifications to normal metabolism, which can lead to several disorders and diseases (Waris and Ahsan, 2006), and eventually to cell death (Jeremy et al., 2004). From a biological perspective, an antioxidant is considered as any compound able to oppose cellular oxidation. Diets rich in fruits and vegetables have been shown to reduce the incidence of cardiovascular disease and some chronic and degenerative diseases associated with oxidative damage (Ames et al., 1993; Dragsted, 2003). The incorporation of fruits and vegetables in the diet may also help to eliminate certain toxins. The protective effects have been associated with the presence of antioxidant compounds (Cao et al., 1996; Wang et al., 1996). Antioxidants are present in all plant organs and include ascorbic acid, carotenoids, vitamin E and phenolic compounds, among others (Larson, 1988) (Figure 5.3). Here we briefly describe some characteristics of these components.

### B. Ascorbic acid

As mentioned before (see Section II.G) ascorbic acid is one of the most important compounds for human nutrition present in fruits and vegetables. The role of AsA in disease prevention has been associated with its capacity to neutralize ROS.



**Figure 5.3** Main dietary antioxidants present in fruits, vegetables and legumes.

### C. Carotenoids

Fruits and vegetables are the main sources of carotenoids in the diet (Rao and Rao, 2007). The presence of conjugated double bonds in carotenoids has a main role in determining their antioxidant properties (Sandmann, 2001). In the last few years, carotenoids have received great attention due to their antioxidant properties and potential to prevent some diseases. The general properties of these compounds were described in Section II.G.

### D. Tocopherols and tocotrienols

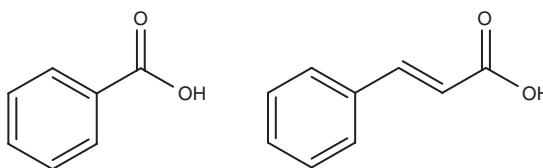
These include the fat-soluble compounds grouped as vitamin E, characterized by a high antioxidant capacity. Their distribution in fruits and vegetables was previously described (see Section II.G).

### E. Phenolic compounds

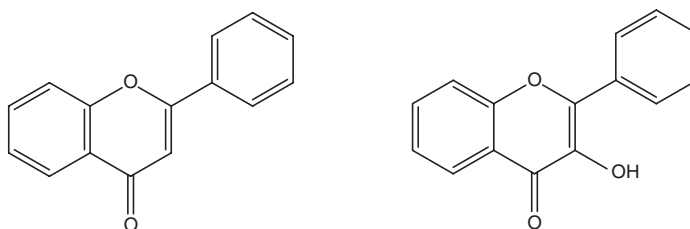
This group encompasses a great diversity of compounds derived from the aromatic amino acids phenylalanine and tyrosine. Their main functions are acting as deterrents of potential predators or antimicrobials, protecting against UV-radiation and contributing to the pigmentation of fruits and flowers. Phenolic compounds can contribute to the astringency and bitter taste of some products. They are generally present in low concentrations, but in certain cases, such as in blueberry, they can reach levels of more than 0.1%. In general, they also accumulate in the peel more than in the pulp of fruits. The general characteristic of the compounds within this group is to have aromatic rings with variable degrees of hydroxylation (Mattila et al., 2006). Phenolic compounds are easily oxidized to quinones. The beneficial properties of berry fruits on human health have been associated in part with the presence of relatively high levels of phenolic compounds (Seeram et al., 2006). There is *in vitro* evidence showing that these compounds could influence several cellular processes. Information regarding the metabolism and effect *in vivo* is much more limited (Duthie et al., 2003). A large number of phenolic compounds have been identified in plants (Tsao and Deng, 2004). They have been subdivided into different subclasses, such as phenolic acids, flavonoids and other compounds (e.g. lignans, stilbenes, tannins, coumarins and lignin).

#### Phenolic acids

Phenolic acids include derivatives of benzoic and cinnamic acid (Benbrook, 2005) (Figure 5.4). The most common benzoic acid derivatives are *p*-hydroxybenzoic, vanillic, syringic and gallic acid, while common cinnamic acid derivatives include *p*-coumaric, caffeic, ferulic and sinapic acid. The derivatives differ in the degree of hydroxylation and methoxylation of the aromatic ring. Caffeic acid is the most abundant phenolic acid in several fruits such as berries (Mattila et al., 2006), while coumaric acid is usually present in lower proportions (Rice-Evans et al., 1997). Ferulic acid represents 90% of total phenolic acids in cereals (Manach et al., 2004; Scalbert and Williamson, 2000). The contribution of each of the phenolic compounds to the



**Figure 5.4** Structure of benzoic acid (left) and cinnamic acid (right), precursors of the two main classes of phenolic acids present in fruits and vegetables.



**Figure 5.5** General structure of flavones (left) and flavonols (right).

antioxidant capacity depends on their structure. For instance, the number of hydroxyls present in the molecule can increase the antioxidant capacity.

### Flavonoids

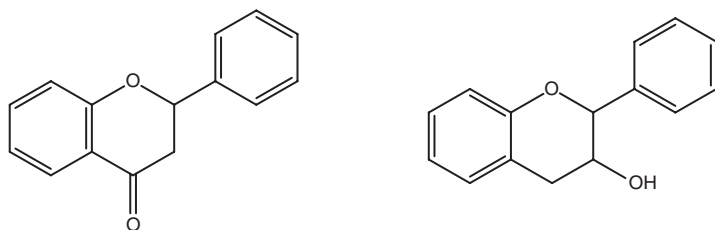
Flavonoids represent a large group of phenolic compounds with two aromatic rings in their structure that are associated together by a 3C-oxygenated heterocycle. Phenolic compounds are usually present as glycosides, which reduce their activity against free radicals and increase their solubility. At the cellular level, they are compartmentalized in the vacuoles (Rice-Evans et al., 1997). There are different classes of flavonoids (Le Marchand, 2002) such as:

- a) flavones and flavanols;
- b) flavanones, flavanols;
- c) isoflavones;
- d) proanthocyanidins; and
- e) anthocyanidins.

**Flavones and flavonols** Flavonols have a central ring of 3-hydroxypyran-4-one (Rice-Evans et al., 1997). Flavones lack the OH in position 3 (Figure 5.5). Rutin, luteolin and apigenin are common among flavones, while the most abundant flavonols are quercetin and kampferol (Manach et al., 2004). Onions are rich in these compounds. Blueberries also have high levels, especially in the peel, because synthesis is stimulated by exposure to light. Celery is a good source of flavones. Flavones are also present in citrus, but they are associated mainly with the fruit peel.

**Flavanones and flavanols** Flavanones do not have the double bond in position 2,3 of the central ring, while flavanols lack the carbonyl group at position 4 (Figure 5.6). The genus *Citrus* is characterized by the accumulation of flavanone glycosides.





**Figure 5.6** General structure of flavanones (left) and flavanols (right).

Orange juice is a source of the flavanone glycoside hesperidin (Tripoli et al., 2007). The flavanols catechin and epicatechin are common in grapes (Rice-Evans et al., 1997).

**Isoflavones** Isoflavones are phytoestrogens present in legumes. Soybean products are a good source of these compounds (Manach et al., 2004). The three most commonly found isoflavones are genistein, glycitein and daidzein.

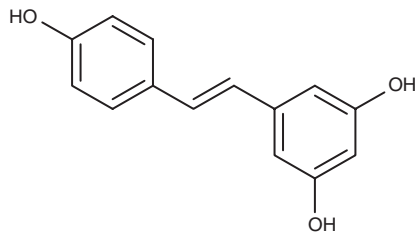
**Proanthocyanidins** Proanthocyanidins are oligomeric flavonoids (usually dimers or oligomers of the flavanols catechin and epicatechin). They are common in the peel and seeds of grapes (Gu et al., 2004). Other sources of these compounds include apple, almond and blueberry.

**Anthocyanidins** Anthocyanidins are pigments giving several fruits their characteristic red or purple colors, although in some conditions they can be uncolored. Besides being pigments, anthocyanidins have great relevance due to their contribution to the antioxidant capacity of fruits and vegetables. The basic structure of anthocyanidins is derived from the flavilium cation (2-phenyl-benzopyril). There are six anthocyanidins more common in fruits and vegetables: pelargonidin, cyanidin, delphinidin, peonidin, petunidin and malvidin. The differences between them are the OH, H and OCH<sub>3</sub> groups associated with the phenolic rings. The distribution of hydroxyls in the molecule influences the antioxidant capacity of the different anthocyanidins. These compounds are usually present as glycosides associated with different sugars, since anthocyanidin glycosylation reduces antioxidant capacity relative to the free aglycons.

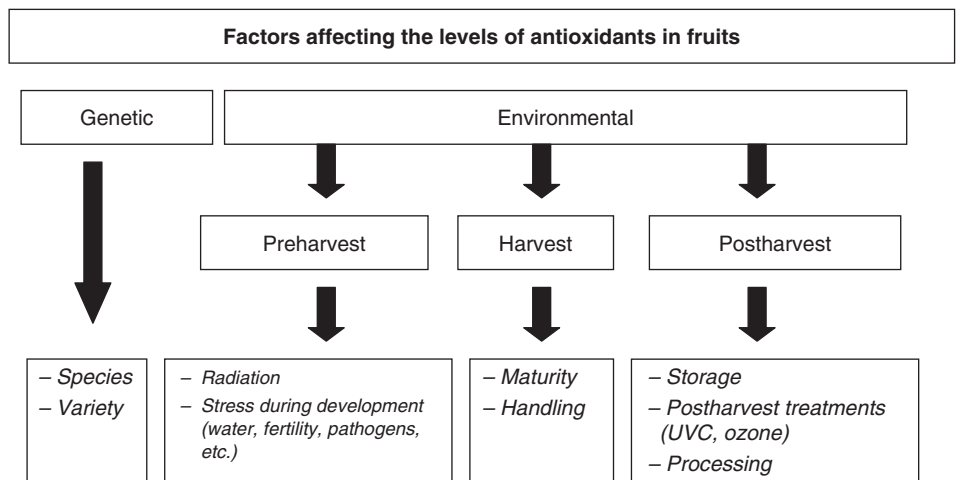
### Others

Lignans are diphenolic structures formed by the association of two derivatives of cinnamic acid (Liu, 2007). They are present mainly in linseeds, cereals and legumes, but their levels are low in fruits and vegetables. Stilbenes are also phenolic compounds described in fruits. The most studied compound in this group is resveratrol (Figure 5.7). This compound has been known for quite a while, and is commonly produced in response to pathogens and other stress conditions in grapes (Langcake and Pryce, 1976). It has also been identified in other fruits, such as blueberry. It has been suggested that it may have anticarcinogenic properties.

Finally, lignin is a phenolic polymer present in secondary cell walls of plant tissues. It is highly hydrophobic and is formed by three main monomeric precursors: coumarylic, sinapyllic and coniferyl alcohols. It is associated with conduction tissues



**Figure 5.7** Resveratrol has been studied in detail in grapes. It has been suggested that this compound has anticarcinogenic properties.



**Figure 5.8** Main factors affecting the level of antioxidants in fruits.

(xylem vessels, sclereids, tracheids), and in general it is not abundant in fruits and vegetables. Its contribution, from the antioxidant point of view, is associated only with the products of its potential degradation that are very limited.

## F. Factors affecting the levels of antioxidants in fruits and vegetables

Several factors influence the accumulation and degradation of antioxidant compounds in fruits. In general terms, these variables could be divided into genetic and environmental. Different factors are included within each of these groups (Figure 5.8).

### Genetic factors

**Species** The species is the first factor determining the prevalence of different antioxidants. Although there are some exceptions, each group is characterized by the accumulation of certain types of antioxidants (Table 5.5). Berries are particularly rich in phenolic compounds (Zheng and Wang, 2003) and vitamin C (Kevers et al., 2007). The main antioxidants in this group seem to be phenolics because, in general, a good correlation between total antioxidant capacity and phenolic compounds has been

**Table 5.5** Fruits and vegetables rich in the different groups of antioxidants

Ascorbic acid	Vitamin E	Carotenoids	Phenolics
Strawberry	Almond	Pineapple	Blueberry
Pepper	Corn	Plum	Plum
Kiwifruit	Broccoli	Peach	Raspberry
Orange	Spinach	Pepper	Strawberry
Pepper	Peanut	Mango	Apple
Broccoli	Avocado	Melon	Blackberry
Guava		Tomato	
Rosehip		Carrot	
Persimmon			

observed. In the case of ripe blueberry, ascorbic acid only contributes 0.4% to 9.0% to the total antioxidant capacity (Kalt et al., 1999).

**Cultivar** For a given species, the levels of antioxidants are also markedly affected by the cultivar considered. For instance, in strawberry, Nelson and co-workers (1972) found variations from 19 to 71 mg of ascorbic acid per 100 g FW in six varieties. Similar differences among varieties have been found for phenolic compounds (Wang and Lin, 2000). The identification of lines or mutants enriched in antioxidants might be useful in breeding programs aimed at improving the nutritional value of fruits and vegetables. The identification of the nature of the genes mutated in lines with altered accumulation of antioxidants might also be of great value. For instance, in the case of tomato the characterization of the high pigment (*hp*) mutants, which accumulate high levels of carotenoids, showed that the mutated gene is associated with plant light responses, and the over-expression of this gene resulted in increased accumulation of carotenoids (Liu et al., 2004). Also, in tomato the level of  $\beta$ -carotene and lycopene were raised by increasing the expression of phytoene synthase and lycopene cyclase, respectively (Fraser et al., 2002; D'Ambrosio et al., 2004). Similarly in carrot, the over-expression of a  $\beta$ -carotene ketolase isolated from *Haematococcus pluvialis* led to the accumulation of the ketocarotenoid astaxanthin (Jayaraj et al., 2008). The generation of transgenic plants has also been seen to increase the levels of other antioxidants such as phenolic compounds. Transformation of tomato with a *Petunia* gene for chalcone isomerase increased the concentration of flavonols in the peel almost 80 times, without altering other phenotypic characteristics (Muir et al., 2001). In the case of ascorbic acid, the elucidation of its biosynthetic pathway opened the way to manipulate ascorbate biosynthesis in plants (Smirnoff, 2000). However, while most of the genes proposed to be involved in these pathways have been cloned and expressed in various plant species, transformation strategies to increase AsA concentrations have had only limited success. Thus, there is a need for alternative approaches to identify the genetic determinants underlying whole plant AsA homeostasis.

#### Environmental factors

**Radiation** In many cases, modifications in the level of phenolic compounds, ascorbic acid and carotenoids have been associated with changes in the radiation interception

in the field. Sun-exposed sides of fruits have higher levels of phenolics and vitamin C than shaded regions (Lee and Kader, 2000). In the case of leafy vegetables, the levels of flavonols are 10 times higher in the surface leaves than in the internal leaves. In tomato, the level of total phenolics increased twofold in plants exposed to higher irradiance. Similarly, these plants presented higher levels of carotenoids and ascorbic acid (Gautier et al., 2008). This illustrates that maximization of radiation interception is important to obtain products with higher accumulation of antioxidants. However, the optimal irradiance levels required to maximize accumulation of the different groups of antioxidants in fruits and vegetables are not well established.

**Cultural practices** There are several works analyzing the effect of cultural practices on the level of different groups of antioxidants. For instance, strawberry fruit grown with plastic mulch had higher antioxidant capacity than fruits from plants grown in beds without plastic mulch (Wang et al., 2002). High nitrogen fertilization has been associated with reduced levels of ascorbic acid (Lee and Kader, 2000), and compost as a soil supplement significantly enhanced levels of ascorbic acid (Wang and Lin, 2003). Vitamin C accumulation also has been inversely correlated with rainfall (Toivonen et al., 1994). Some authors have found evidence suggesting that organic products might accumulate higher levels of antioxidants and vitamins than those produced conventionally (Woese et al., 1997; Weibel et al., 2000; Asami et al., 2003; Chassy et al., 2006). However, there are also studies that show either results that are opposite, or results that show no difference (Barrett et al., 2007). Winter and Davis (2006) concluded that it is not possible to ensure that, from a nutritional point of view, organically grown products are superior to those obtained by conventional agricultural techniques.

**Maturity at harvest** The developmental stage might affect the antioxidant capacity of fruits (Prior et al., 1998). The nature of these changes depends on the product considered. For instance, in tomato and pepper total antioxidant capacity increases because of the accumulation of carotenoids and vitamin C. In the case of blueberry fruit the concentration of phenolic acids decreases during ripening, while anthocyanins are accumulated (Castrejón et al., 2008), resulting in a net reduction of total antioxidant capacity during development. Similar patterns have been observed in strawberry and blackberry (Wang and Lin, 2000). In the case of carotenoids, in some products (e.g. pepper, tomato, mango) the concentration increases during development (de Azevedo and Rodriguez-Amaya, 2005). In contrast, products in which color is mainly associated with the accumulation of anthocyanins or products that maintain their green color at harvest usually show a reduction in the level of carotenoids as development progresses (Rodriguez-Amaya, 2001).

**Wounding** Mechanical damage may cause alterations in the levels of antioxidants. In the case of AsA, cellular breakage causes an increase in the levels of the internal pressure of oxygen favoring oxidation. Carotenoid degradation is also accelerated by oxygen, but the stability of these compounds is higher than that of AsA. In the case of phenolic compounds, wounding could alter both their synthesis and degradation (Tomás-Barberán et al., 1997; Loaiza Velarde et al., 1997). In lettuce, wounding led to the accumulation of soluble phenolic compounds (e.g. chlorogenic acid) (Choi et al., 2005). From a molecular perspective, wounding has been shown to induce *de novo*

synthesis of phenylalanine ammonia lyase, a key enzyme in phenylpropanoid metabolism (Choi et al., 2005). Besides its role on phenolic biosynthesis, wounding also affects degradation. First, also in response to wounding, an increase in enzymes associated with phenolics oxidation such as polyphenol oxidases (PPOs) and peroxidases (PODs) has been reported. In addition, cell disruption allows direct contact between pre-existing phenolic degrading enzymes. Finally, the production of hydrogen peroxide upon damage provides a secondary substrate of PODs and the reduction of barriers for oxygen diffusion might favor PPO activity. This might promote the oxidation of phenolics, which can then polymerize, leading to the formation of brown colored pigments that may ultimately reduce quality. Consequently, careful handling and minimization of physical damage is recommended.

**Storage** The effect of storage on antioxidants in many cases is related to the role of ethylene in the ripening process. Consequently, the final effect on antioxidant (AOX) levels will depend on the typical modifications observed during development of the species considered. In some cases, ethylene can induce specific antioxidants. For instance, in carrot, ethylene stimulated the accumulation of an isocoumarin (6-methoxymellein). In berries it has been observed that atmospheres with high levels of oxygen (60% and 100%) result in increased antioxidant capacity by favoring anthocyanins and other phenolics accumulation (Zheng et al., 2003). However, the oxidation of AsA might also be favored in these conditions. Besides the effect of any specific group of antioxidants in most fruits, it has been observed that the changes in total antioxidant capacity are not dramatic during postharvest storage. Excluding some products, such as broccoli and banana, fruits and vegetables, in general, lose their visual quality before marked losses in total antioxidants occur (Kevers et al., 2007). In some cases, an increase in total AOX capacity is observed, basically, associated with the accumulation of phenolics. In strawberry, storage at 5°C and 10°C increased the antiradical capacity (Ayala-Zavala et al., 2004). Further studies to evaluate the extent of this increased accumulation of antioxidants in some fruits might be done to determine the potential for increasing the functionality of fruits and vegetables through manipulation of the postharvest environment (Kalt et al., 1999).

**Other treatments** Some studies suggest that manipulation of the metabolism of products by the application of postharvest treatments could be useful to increase the antioxidant capacity, with consequent nutritional benefit (Kalt et al., 1999). Phenolic compounds' synthesis might be triggered in response to stress conditions, such as infection by microorganisms or wounding, ultraviolet (UV) irradiation or the exposure of the products to ozone-enriched atmospheres. In grapes, postharvest UV-C and ozone treatments increased the accumulation of resveratrol (Cantos et al., 2001; Versari et al., 2001; Gonzalez-Barrio et al., 2006). The elicitation of the accumulation of antioxidant compounds has also been observed in other fruits. In blueberry cv. Bluecrop, besides reducing decay, UV-C radiation exposure (2 or 4 kJ/m<sup>2</sup>) resulted in increased accumulation of anthocyanins and higher levels of antioxidants (Perkins-Veazie et al., 2008). In the case of strawberry, UV-C treatments also increased the level of phenolic compounds and the antiradical capacity (Ayala-Zavala et al., 2004). These results, at a laboratory scale, show an interesting eliciting effect of some

postharvest treatments on antioxidant accumulation. Further studies would be useful to determine the potential of these strategies on a commercial scale.

**Processing** The effect of processing on the level and bioavailability of antioxidants depends on the treatment intensity, as well as on the component considered (Bernhardt and Schlich, 2006). In some cases, processing could lead to higher availability of antioxidants, due to an increase in the ease of extractability. For instance, with carrot and spinach carotenoids vapor cooking increases assimilation, probably due to a disruption of carotenoid-protein complexes. Similarly, the bioavailability of lycopene increases in heat-treated tomato. However, cooking could cause the isomerization of  $\beta$ -carotene, leading to the formation of *cis* isomers with lower provitamin A activity (Deming et al., 2002a,b). For instance, in the case of fresh carrots, 100% of the  $\beta$ -carotene is present in the *trans* form, while canning results in a significant formation of *cis* isomers. Carotenoids are in general susceptible to oxidation. Heat, light and oxygen could accelerate their degradation (von Elbe and Schwartz, 1996). Minimizing the influence of these factors could reduce carotenoids loss. Ascorbic acid is one of the antioxidants more susceptible to degradation. Blanching or even freezing and thawing could cause losses up to 25%. More drastic treatments could lead to losses of up to 90% of AsA. Some of the factors affecting the loss of AsA include the degree of heating, the exposed surface (which affects lixiviation in the cooking media), oxygen levels and product pH (Eitenmiller and Landen, 1999). The stability of AsA could be increased at low pH, reduced oxygen pressure, darkness and presence of chelating agents. Consumption in the fresh state is the best way to minimize AsA losses. Finally, processing can also cause losses of phenolic antioxidants. For instance, peeling or cutting reduces quercetin levels by only 1%, but cooking in water may reduce the content of this component by 75%.

#### **IV. Fruits and vegetables as direct sources of minerals**

Dietary minerals raise concern for health specialists and consumers, due to the number of processes they are involved in and the continuous research highlighting the benefits of their adequate and balanced intake. Although there is no universally accepted definition or classification, the dietary focus on “minerals” derives from an interest in supporting the biosynthetic apparatus with required elemental components other than carbon, hydrogen and oxygen.

Total mineral content is determined by the ash value. Nevertheless, classification of many elements as essential minerals for human nutrition is not definitive, and there is still debate as to the natural biological role of vanadium, chromium, boron, aluminum and silicon in human health. Minerals are normally classified as macro- or micronutrients, based on the relative concentration of each nutrient when those concentrations are adequate for normal tissue function. Macronutrients include potassium (K), calcium (Ca), magnesium (Mg), nitrogen (N), and phosphorus (P), and their concentrations in plant tissues range from 1000 to 15 000  $\mu\text{g}$  per gram of dry weight. In contrast, the concentrations of micronutrients usually found in plant

tissues are 100- to 10000-fold lower than those of macronutrients. Mineral micronutrients considered essential in human nutrition include manganese (Mn), copper (Cu), iron (Fe), zinc (Zn), cobalt (Co), sodium (Na), chlorine (Cl), iodine (I), fluorine (F), sulfur (S), and selenium (Se). Macronutrients can also be classified into those that maintain their identity as ions within plant tissues (e.g.  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ ), and those that are assimilated into organic compounds (e.g. N and P).

In general, vegetables are a richer source of minerals than fruits, but both vegetables and fruits are considered “nutrient-dense foods” in that they provide substantial amounts of micronutrients, such as minerals and vitamins, but relatively few calories (Table 5.6).

Minerals have both direct and indirect effects on human health. The direct effects of minerals focus on the consequences of their consumption on human nutrition, while the indirect effects refer to their incidence in fruit and vegetable quality and subsequent consumer acceptance. From a direct nutrition standpoint, potassium has the biggest presence in both fruits and vegetables, but nitrogen and calcium show major impacts on horticultural crop quality.

**Table 5.6** Fruit and vegetable sources of potassium, ranked by milligrams of potassium per standard amount, also showing calories in the standard amount\*. The dietary reference intake (DRI) for potassium for adults and adolescents is 4700 mg/day.

Fruits and vegetables, standard amount	Potassium (mg)	Calories
Sweetpotato, baked, 1 potato (146 g)	694	131
Tomato paste, ¼ cup	664	54
Beet greens, cooked, ½ cup	655	19
Potato, baked, flesh, 1 potato (156 g)	610	145
White beans, canned, ½ cup	595	153
Tomato puree, ½ cup	549	48
Prune juice, ¾ cup	530	136
Carrot juice, ¾ cup	517	71
Lima beans, cooked, ½ cup	484	104
Winter squash, cooked, ½ cup	448	40
Banana, 1 medium	422	105
Spinach, cooked, ½ cup	419	21
Tomato juice, ¾ cup	417	31
Tomato sauce, ½ cup	405	39
Peaches, dried, uncooked, ¼ cup	398	96
Prunes, stewed, ½ cup	398	133
Apricots, dried, uncooked, ¼ cup	378	78
Cantaloupe, ¼ medium	368	47
Honeydew melon, ⅛ medium	365	58
Plantains, cooked, ½ cup slices	358	90
Kidney beans, cooked, ½ cup	358	112
Orange juice, ¾ cup	355	85
Split peas, cooked, ½ cup	355	116

\*US Department of Health and Human Services and US Department of Agriculture, 2005.

Until recently, nutrition research focused on single-mineral impact on human health, generally with incongruent results. The recognition that minerals are not consumed individually, but as combined constituents of a varied diet, has shifted the efforts in this area to unraveling the role of the overall diet, or dietary patterns, in blood pressure and cardiovascular diseases, bone diseases and a range of chronic disorders. Epidemiological surveys suggest that the total diet has a greater influence on health than do specific components. From these dietary pattern studies, it has become increasingly clear that it is not merely the excess or deficiency of a single mineral, but also deficiencies of multiple nutrients in combination that have the greatest dietary effects on health. Adequate intake of minerals such as potassium – specifically derived from foods such as horticultural crops, where they coexist with other essential nutrients – contributes to overall health.

As described in previous sections, fruits and vegetables provide a milieu of phytochemicals, non-nutritive substances that possess health protective benefits. In contrast, fruits and vegetables may not usually be recognized as primary sources of mineral intakes from a nutritional point of view (Fairweather-Tait and Hurrell, 1996). Nevertheless, the Dietary Approaches to Stop Hypertension (DASH) emphasize fruit, vegetable and low-fat dairy product consumption as a source of minerals. In the DASH dietary pattern, vegetables contribute an average of 14.3%, 15.5%, 16.2% and 10.4% to the intakes of calcium, magnesium, potassium and zinc, respectively (Lin et al., 2003). Correspondingly, fruits and juices contribute an average of 5.8%, 17.3%, 33.0% and 6.6% (Lin et al., 2003).

There has been a natural trend towards lower mineral content in fruits and vegetables over the past decades (Mayer, 1997; Ekholm et al., 2007) which have not been fully compensated for by the increase in fruit and vegetable consumption. Vegetable contribution of potassium, phosphorus, magnesium, calcium, copper, iron and zinc to the US food supply significantly decreased during the last century, while fruit contribution of potassium, phosphorus, magnesium and copper increased (Table 5.7).

**Table 5.7 Minerals (%) contributed from fruits and vegetables to the US food supply in selected years**

Mineral	Fruit			Vegetables		
	Year/s			Year/s		
	1909–1919	1960–1969	2004	1909–1919	1960–1969	2004
Potassium	8.0	8.7	11.2	36.7	27.1	26.6
Calcium	2.6	2.2	2.6	8.7	6.0	7.0
Phosphorus	1.5	1.5	1.8	10.4	7.7	7.7
Magnesium	4.5	5.6	6.1	18.2	15.9	13.9
Copper	5.2	6.1	6.1	30.2	22.8	17.2
Iron	3.3	3.1	2.5	18.4	13.5	10.1
Zinc	1.2	1.3	1.2	9.1	7.4	6.4
Sodium	0.8	1.3	2.0	10.4	23.4	28.9
Selenium	0.5	0.6	0.4	1.2	2.4	2.3

Source: Hiza and Bente, 2007.



Nowadays different postharvest strategies for improving the mineral intake from fruits and vegetables are being implemented. These comprise increasing consumption of fruits and vegetables and increasing levels of essential nutrients through fortification methods. Alternative approaches include improving nutrient bioavailability and retention.

## A. General considerations of selected minerals

### Potassium (K)

A potassium-rich diet contributes to lower blood pressure, blunting the effects of salt (Salunkhe et al., 1991). Inadequate levels of potassium intake have long been associated with higher blood pressure (McCarron and Reusser, 2001). Potassium also regulates heartbeat, assists in muscle contraction and is needed to send nerve impulses and to release energy from fat, carbohydrates and protein. Different nutrients and phytochemicals in fruits and vegetables, including potassium, may be independently or jointly responsible for an apparent reduction in cardiovascular disease risk (Ignarro et al., 2007). Potassium is a systemic electrolyte and is essential in coregulating ATP with sodium. Potassium favorably affects acid–base metabolism, which may reduce the risk of developing kidney stones (Zerwekh et al., 2007), and possibly decrease bone loss with age. Although calcium intake is an important determinant in peak bone mass, and in retarding bone loss in postmenopausal women, findings of higher bone mass and lower bone resorption in women consuming high intakes of potassium, magnesium, zinc and vitamin C emphasizes the importance of considering the impact of variation in other nutrients when focusing on a particular mineral (Cohen and Roe, 2000). In fact, up to 11 different groups of compounds (vitamins, minerals, antioxidants and others) in fruits and vegetables could influence bone health (MacDonald, 2007).

Potassium is the most abundant individual mineral element in fruits and vegetables. It normally varies between 60 and 600 mg per 100 g<sup>-1</sup> of fresh tissue. It plays a role in a myriad of cellular and whole plant functions: it serves as an osmoticum for cellular growth and stomatal function, balancing the charges of anions, activating almost 60 plant enzymes and participating in numerous metabolic processes, including protein synthesis, oxidative metabolism and photosynthesis.

In fruits and vegetables, potassium occurs mainly in combination with various organic acids. Examples of potassium-rich fruits and vegetables include bananas and plantains, leafy green vegetables, many dried fruits, oranges and orange juice, cantaloupes and honeydew melons, tomatoes and root vegetables (Table 5.7).

### Calcium (Ca)

Calcium is essential for bone and tooth formation. Because of this, calcium requirements are higher during adolescence. Calcium is also very important during later adulthood, and of great consequence from a public health perspective, because inadequate intake of calcium may increase the risk of osteoporosis, a condition in which decreased bone mass weakens bone (Nordin, 1997; Cohen and Roe, 2000). With nearly half of all American women over 50 years of age demonstrating low

mineral bone density or osteoporosis, and an estimated 1.3 million osteoporosis-related fractures occurring each year in the US, with a billion dollar estimated annual cost (DeBar et al., 2004), osteoporosis prevention is a major public health target. Calcium fluxes are important mediators of hormonal effects on target organs through the phosphoinositol system, and are closely linked with the cyclic AMP systems. There is also evidence linking hypertension with calcium deficiency (Appel et al., 1997; McCarron and Reusser, 2001).

In plants, calcium is primarily associated with the pectic materials. It is believed to have a major influence on the rheological properties of the cell wall and, consequently, on the texture and storage life of fruits and vegetables.  $\text{Ca}^{2+}$  can interact with the anionic pectic polysaccharides, coordinating with the oxygen functions of two adjacent pectin chains to form the so-called “eggbox structure,” and cross-linking the chains (Rose et al., 2003). Intracellular  $\text{Ca}^{2+}$  also occupies a pivotal role in cell signal transduction (Sanders et al., 1999). The plant signals thought to be transduced through cytosolic  $\text{Ca}^{2+}$  include wounding, temperature stress, fungal elicitors, oxidative stress, anaerobiosis, abscisic acid, osmotic stress, red or blue light and mineral nutrition. Intracellular  $\text{Ca}^{2+}$  transient increases are often associated with initiation of responses. Thus,  $\text{Ca}^{2+}$  is a prominent second messenger, and it must be maintained in the cytoplasm at concentrations many orders of magnitude lower than the  $\text{Ca}^{2+}$  in the cell wall.

Horticultural crops are considered a secondary source of calcium in comparison to dairy products but, taken as a whole, fruits and vegetables account for almost 10% of the calcium in the US food supply (Table 7, Cook and Friday, 2003). Dark green leafy cabbage family vegetables and turnip greens are good calcium sources and most green leafy vegetables are potential calcium sources because of their absorbable calcium content (Jodral-Segado et al., 2003; Titchenal and Dobbs, 2007). Projects designed to test the efficacy of a health plan-based lifestyle intervention for increasing bone mineral density propose not only to increase the consumption of high calcium foods, but also of fruits and vegetables (DeBar et al., 2004).

### **Magnesium (Mg)**

Magnesium is important in protein synthesis, release of energy from muscle storage and body temperature regulation. It is critical for proper heart function and plays a role in bone formation, as previously described. Magnesium activates over 100 enzymes.

In plants, magnesium is a constituent of the chlorophyll molecule: the porphyrin-like ring structure of chlorophylls contains a central magnesium atom coordinated to the four pyrrole rings. On the other hand, magnesium is involved in the energetic metabolism as a constituent of the Mg-ATP or Mg-ADP complex. Also, the Calvin cycle – the pathway that produces a three-carbon compound as the first stable product in the multistep conversion of  $\text{CO}_2$  into carbohydrates – is partially regulated via stromal  $\text{Mg}^{2+}$  concentration. This nutrient also serves important biochemical functions in protein synthesis (Mengel and Kirkby, 1982).

In 2004, vegetable contribution to the total magnesium in the US food supply was an average of 14% (Table 5.7). Using current population standards, magnesium

intake was found to be below adequate levels for both adults and children (Sigman-Grant et al., 2003). Mixed users, who are more likely to consume higher intakes of grains, fruit and milk products, were found to have higher magnesium densities than high-fat users, who consume significantly more servings of meat and higher levels of discretionary fat (Sigman-Grant et al., 2003). Generally, magnesium levels are significantly higher in vegetables than in fruits, but nuts are good sources of this nutrient. Dry fruits and legumes are the food groups that rank higher in magnesium content (Jodral-Segado et al., 2003).

### **Phosphorus (P)**

Inorganic phosphate is essential for skeletal mineralization and for multiple cellular functions, including glycolysis, gluconeogenesis, DNA synthesis, RNA synthesis, cellular protein phosphorylation, phospholipid synthesis and intracellular regulatory roles (DiMeglio et al., 2000). Phosphorus is a primary bone-forming mineral. In western countries, isolated dietary phosphate deficiency is exceedingly rare, because most westerners eat high-phosphate diets, except for occasional metabolic disorders such as hyperphosphatemia (DiMeglio et al., 2000).

Phosphorus can exist in plants as both inorganic phosphate anions and organophosphate compounds (Raghothama, 1999). Unlike sulfate and nitrate, phosphate is not reduced in plants during assimilation, but remains in its oxidized state forming phosphate esters in a wide variety of organic compounds. Inorganic phosphorus constitutes a main structural component of nucleic acids and phospholipids, and plays a critical role in energy conversion in the form of high-energy phosphoester and diphosphate bonds. It is important both as a substrate and as a regulatory factor in oxidative metabolism and photosynthesis, it participates in signal transduction, and regulates the activities of an assortment of proteins by way of covalent phosphorylation/dephosphorylation reactions.

In 2004, the primary contributor of phosphorus to the food supply was the dairy group (31.3%), followed by the meat, poultry and fish group (24.9%) and grain products (19.4%) (Hiza and Bente, 2007). Fruit and vegetable contribution to the total phosphorus in the US food supply was an average of 9.5% (Table 5.7). Among tree fruits, nuts are natural sources of phosphorus.

### **Nitrogen (N)**

The largest requirement for nitrogen in eukaryotic organisms is the biosynthesis of amino acids, building blocks of proteins and precursors of many other compounds. Proteins represent a large percentage of the human body and carry out many different cell functions. Therefore, protein synthesis is central to cell growth, differentiation, and reproduction.

Nitrogen is also an essential component of nucleic acids, cofactors and other metabolites. Several plant hormones (indole-3-acetic acid, zeatine, spermidine, etc.) contain nitrogen, or are derived from nitrogenous precursors. Alkaloids and other secondary compounds contain nitrogen, and various phenolics derive from phenylalanine and are therefore linked with amino acid metabolism. Moreover, nitrogen is a major constituent of chlorophyll. The characteristic preharvest yellow color of

nitrogen-starved vegetables – a physiological disorder called chlorosis – reflects their inability to synthesize adequate amounts of green chlorophyll under nitrogen-limited conditions.

### **Sulfur (S)**

Sulfur is an essential nutrient required for growth, primarily used to synthesize cysteine and methionine. The sulfur-containing amino acids play pivotal roles in the structural and catalytic functions of proteins. Cysteines are important because oxidizing the thiol groups of two cysteine residues can form disulfide bonds, important covalent linkages involved in establishing tertiary and, in some cases, quaternary protein structures. The dithiol↔disulfide interchange can be a regulatory mechanism, as well as a mediator of redox reactions. Sulfur is also a component of numerous essential and secondary metabolites derived from these amino acids.

Sulfur nutrition is important in the species within the order Brassicales (e.g. white cabbage, broccoli, cauliflower, capers) for the synthesis of anticarcinogenic glucosinolate compounds (reviewed in Sozzi, 2001). In caper (*Capparis spinosa* L.) flavor, 160 components were identified, including elemental sulfur (S<sub>8</sub>) and more than 40 sulfur-containing compounds, among them thiocyanates and isothiocyanates.

Although of key importance in human and plant life, sulfur is a relatively minor component in comparison with nitrogen. Generally, it is not a growth-limiting nutrient, since sulfate, the oxidized anion, is relatively abundant in the environment.

### **Manganese (Mn)**

Manganese is a key component of enzyme systems, including oxygen-handling enzymes. It supports brain function and reproduction and is required for blood sugar regulation. In addition, it is part of bone structure. Manganese is a cofactor in function of antioxidant enzymes, such as the mitochondrial superoxide dismutase.

In plants, manganese atoms appear to undergo successive oxidations to yield a strongly oxidizing complex that is capable of water oxidations during photosynthesis. Also like magnesium, manganese is required in enzyme reactions involving carbon assimilation. Chloroplasts are most sensitive to manganese deficiency. Among horticultural crops, spinach is a good source of manganese.

### **Copper (Cu)**

Copper, a redox active metal, plays an important role in the oxidative defense system. In fact, oxidative stress is a characteristic of copper deficiency (Uriu-Adams and Keen, 2005). Copper is necessary for the formation of hemoglobin and is required for the function of over 30 proteins, including superoxide dismutase, ceruloplasmin, lysyl oxidase, cytochrome c oxidase, tyrosinase and dopamine-β-hydroxylase (Arredondo and Nuñez, 2005). During the past decade, there has been increasing interest in the concept that marginal deficits of this essential nutrient can contribute to the development and progression of a number of disease states, including cardiovascular disease and diabetes. Deficits of this nutrient during pregnancy can result in gross structural malformations in the fetus, and persistent neurological and immunological abnormalities in the offspring (Uriu-Adams and Keen, 2005).

In plants, copper is required for chlorophyll synthesis and in several copper-containing enzymes involved in the reduction of molecular oxygen. The availability of copper to plants, as with other trace minerals, markedly decreases as pH rises above seven. At high pH copper is strongly adsorbed to clays, iron and aluminum oxides, and organic matter. Of the micronutrients required by plants, copper often has the lowest total concentration in soil.

Between 1909 and 1919 in the US, the vegetable group was the leading source of copper (30%). In 2004, the grain group (21%) and the legumes, nuts and soy group (20%) replaced the vegetable group (17%) as the leading sources of copper (Table 7, Hiza and Bente, 2007).

### **Iron (Fe)**

The metabolic fates of copper and iron are intimately related. The essentiality of iron, as well as that of copper, resides in its capacity to participate in one-electron exchange reactions. Systemic copper deficiency generates cellular iron deficiency that, in humans, results in diminished work capacity, reduced intellectual capacity, diminished growth, alterations in bone mineralization, and diminished immune response. Iron is required in numerous essential proteins, such as the heme-containing proteins, electron transport chain and microsomal electron transport proteins, and iron-sulfur proteins and enzymes such as ribonucleotide reductase, prolyl hydroxylase phenylalanine hydroxylase, tyrosine hydroxylase and aconitase (Arredondo and Nuñez, 2005).

Iron is a constituent of the haem complex, a naturally occurring plant chelate involved in electron transfer in a number of important plant enzymes (Mengel and Kirkby, 1982). The plant plastid stroma may contain deposits of phytoferritin, a storage form of iron similar to the ferritin of animal cells. Phytoferritin occurs almost exclusively in plastids and most abundantly in the plastids of storage organs (Briat and Lobreaux, 1997). In green vegetable leaves, there is a good correlation between iron supply and chlorophyll content. Inadequate iron nutrition results in abnormal chlorophyll development, so that deficiency begins as an interveinal chlorosis on younger leaves resulting in prominent green veins. The resultant reduction in photosynthetic capability also reduces the weight and area of affected leaves. Descriptions of causes of iron deficiency have been extensively reviewed for horticultural crops (Korcak, 1987).

Adult users of lower-fat foods consume more nutrient-dense diets, with higher intakes of iron (Kennedy et al., 2001; Sigman-Grant et al., 2003). The predominant source of iron in the American food supply is grain products, followed by the meat, poultry and fish group. Between 1909 and 1919, the vegetable group furnished an average of 18% of the iron in the food supply, but in 2004 that share dropped to an average of 10% (Table 5.7). This is partially due to a decrease in the use of white potatoes after 1920. Although potatoes are not a good source of iron, their contribution to the food supply increases when eaten in large quantities (Hiza and Bente, 2007), particularly if the skin is consumed (specifically, baked potato skin is 20-fold richer in iron than the flesh). Almonds, pistachio nuts, walnuts, pecans, etc., are very good sources of iron. Different vegetables (e.g. parsley, broccoli, kale, turnip greens and collards) and legumes (e.g. green peas and beans) are also considered good sources of iron.

**Zinc (Zn)**

Zinc is a pervasive microelement that plays a catalytic or a structural role in more than 200 enzymes (e.g. carboxypeptidase, liver alcohol dehydrogenase and carbonic anhydrase) involved in digestion, metabolism, reproduction, and wound healing.  $Zn^{2+}$  is a cation with various coordination possibilities and several potential geometries. Thus, it is easily adaptable for different ligands. The main role of structural  $Zn^{2+}$  in proteins is to stabilize tertiary structures. In addition, zinc has a critical role in immune response, and is an important antioxidant.

Zinc activates a number of plant cell enzymes (Romheld and Marschner, 1991), but only a few of them (i.e. alcohol dehydrogenase, superoxide dismutase, carbonic anhydrase, RNA polymerase) contain the micronutrient. Zinc can affect carbohydrate metabolism because different Zn-dependent enzymes participate in biochemical reactions involving sugars. Zinc also plays a role in the maintenance of cell membrane integrity, in the protection from  $O_2^{\cdot-}$  damage, and the synthesis of RNA and tryptophan, a precursor of indole-3-acetic acid. A comprehensive review of soil, plant and management factors associated with zinc nutrition in horticultural crops has been developed by Swietlik (1999).

Fruits and vegetables account for only 1.2% and 6.4%, respectively, of the zinc in the American food supply (Hiza and Bente, 2007). As is the case for magnesium, zinc intakes may be below the adequate levels for both adults and children (Sigman-Grant et al., 2003). Fruits are poor in zinc, but pecans and walnuts are good sources of this essential mineral. Parsley is also a good source of zinc.

**Sodium (Na)**

Sodium is a systemic ion. It is important in electrolyte balance and essential in coregulating ATP with potassium. In addition, it has an important role in the regulation of blood pressure.

Sodium contributed from vegetables increased during the last decades (Table 5.7), due to the increased consumption of processed vegetables (largely tomatoes and white potatoes). With the exception of canned vegetables, sodium estimates in the food supply do not account for sodium added in processing. Thus, the relative contribution of vegetables to sodium reported in the food supply is likely overstated (Hiza and Bente, 2007). Table salt (NaCl) is by far the main dietary source for sodium. Olives and spinach are horticultural sources of sodium. In general, fruits are poor in sodium, and are recommended for low-sodium dietary patterns.

**B. Factors influencing mineral content of fruits and vegetables****Influence of the species and the cultivar**

Mineral composition varies widely in raw fruits (Table 5.8) and vegetables because of genetics. Leafy vegetables tend to have higher concentrations of nutrients that are less mobile in the plant (e.g. calcium) and depend on direct water flow rather than recycling from leaves. Tissues with higher transpiration rates generally have higher tissue calcium concentrations (Witney et al., 1990b). Concentrations of minerals may also vary widely with the cultivar. For example, both Dwarf Brazilian bananas

**Table 5.8** Mineral composition of a range of fruit species. Results are in mg 100 g<sup>-1</sup> fresh weight.

Fruit	Mineral									
	K	Ca	Mg	P	Mn	Cu	Fe	Zn	Na	Se
Apples, raw, with skin	107	6	5	11	0.035	0.027	0.12	0.04	1	0.0
Apricots, raw	259	13	10	23	0.077	0.078	0.39	0.2	1	0.1
Avocado, raw (California)	507	13	29	54	0.149	0.170	0.61	0.68	8	0.4
Avocado, raw (Florida)	351	10	24	40	0.095	0.311	0.17	0.4	2	-
Bananas, raw	358	5	27	22	0.270	0.078	0.26	0.15	1	1.0
Blackberries, raw	162	29	20	22	0.646	0.165	0.62	0.53	1	0.4
Blueberries, raw	77	6	6	12	0.336	0.057	0.28	0.16	1	0.1
Cherries, sweet, raw	222	13	11	21	0.070	0.060	0.36	0.07	0	0.0
Figs, raw	232	35	17	14	0.128	0.070	0.37	0.15	1	0.2
Grapefruit, raw, pink and red (California and Arizona)	147	11	9	12	0.020	0.032	0.08	0.07	1	-
Grapefruit, raw, pink and red (Florida)	127	15	8	9	0.010	0.044	0.12	0.07	0	1.4
Grapes, red or green (euro type, e.g. "Thompson seedless"), raw	191	10	7	20	0.071	0.127	0.36	0.07	2	0.1
Kiwifruit, fresh, raw	312	34	17	34	0.098	0.130	0.31	0.14	3	0.2
Lemons, raw, without peel	138	26	8	16	0.030	0.037	0.60	0.06	2	0.4
Mangos, raw	156	10	9	11	0.027	0.110	0.13	0.04	2	0.6
Melons, Cantaloupe, raw	267	9	12	15	0.041	0.041	0.21	0.18	16	0.4
Oranges, raw, California, "Valencia"	179	40	10	17	0.023	0.037	0.09	0.06	0	-
Papayas, raw	257	24	10	5	0.011	0.016	0.10	0.07	3	0.6
Peaches, raw	190	6	9	20	0.061	0.068	0.25	0.17	0	0.1
Pears, raw	119	9	7	11	0.049	0.082	0.17	0.10	1	0.1

(Continued)

Table 5.8 Continued

Fruit	Mineral									
	K	Ca	Mg	P	Mn	Cu	Fe	Zn	Na	Se
Pineapples, raw, all varieties	109	13	12	8	0.927	0.110	0.29	0.12	1	0.1
Plums, raw	157	6	7	16	0.052	0.057	0.17	0.10	0	0.0
Pomegranates, raw	259	3	3	8	–	0.070	0.30	0.12	3	0.6
Raspberries, raw	151	25	22	29	0.670	0.090	0.69	0.42	1	0.2
Strawberries, raw	153	16	13	24	0.386	0.048	0.41	0.14	1	0.4
Watermelon, raw	112	7	10	11	0.038	0.042	0.24	0.10	1	0.4

US Department of Agriculture, 2008.

(Santa Catarina Prata, *Musa* sp. AAB) and Williams (Cavendish subgroup, *Musa* sp. AAA) are considered as a good source of potassium. Nevertheless, Dwarf Brazilian bananas have higher P, Ca, Mg, Mn and Zn contents than Williams bananas (Wall, 2006). In contrast, no strawberry variety was statistically superior as a source of minerals (Hakala et al., 2003).

Because of the distribution of vascular tissue, sink characteristics and metabolic rates, higher mineral concentrations are usually found in the skin and seeds, with lower concentrations in the flesh of fruits. Tissues with higher metabolic rates (epi-carp, core) may have higher requirements for nitrogen and phosphorus. Rapidly expanding or large-celled tissues are unlikely to have high calcium concentrations. In mature fruit, the calcium concentration is highest in the peel (Saure, 2005).

#### Influence of preharvest factors and practices

Orchard location has proved to have important effects on fruit and vegetable mineral content (Table 5.8). For example, potassium content in bananas markedly differs between different locations in Hawaii, from 288 mg 100 g<sup>-1</sup> in Kapaa to 485 mg 100 g<sup>-1</sup> in Waimanalo (Wall, 2006). Papaya cv. Rainbow is not very rich in potassium, but its content also varies between locations, from 113 mg 100 g<sup>-1</sup> on the island of Hawaii to 203 mg 100 g<sup>-1</sup> on the island of Maui (Wall, 2006).

Mineral composition fluctuates widely in raw fruits and vegetables, because of preharvest factors (soil fertility – including pH and availability of nutrients – moisture content of the soil, growth temperature) and cultural practices (amount and timing of fertilization and irrigation, application of plant growth regulators, pruning and thinning of tree fruit species, etc.). Most of these practices have been established primarily for productivity goals, and not as a medium to better human health, horticultural crop postharvest life or flavor quality (Crisosto and Mitchell, 2002). Usually, fertilizers are applied directly to the soil to raise nutrient levels, if they are inadequate for



the successful growth of the crop, and to maintain soil fertility, which will decline if nutrient removal from the soil (via crop uptake, leaching, volatilization or denitrification) exceeds nutrients added via weathering of minerals and mineralization of organic matter. Nitrogen is the most frequently deficient and most commonly applied fertilizer in orchards, while addition to the soil of phosphorus and potassium is warranted when soil-test results, plant response or tissue analysis indicate a requirement. N-P-K addition with irrigation water (fertigation) has several advantages, including the ability to transport soluble nutrients directly to the root zone whenever the plant is watered. Thus, fertilizer amounts and timing can be precise and adjusted to coincide more closely with actual plant demand. Calcium additions can be large when lime is applied to increase soil pH. Most micronutrients are rarely applied via soil and can be directly supplied via spray application of dilute concentrations of minerals to the canopy. In the case of fruits, the quantity of nutrients capable of being absorbed through the waxy cuticle is often small relative to nutrient demand, but can ameliorate deficiency symptoms and improve fruit quality (Swietlik and Faust, 1984).

An excessive supply of nutrients relative to photosynthesis can develop when the rate of nutrient assimilation is high relative to net photosynthesis. In this case, an accumulation of nutrients in fruits and vegetables can reach levels that are toxic either to the plant or to consumers. For example, excessive nitrogen application can lead to potentially harmful accumulations of nitrate nitrogen, especially in leafy greens and potatoes (Eppendorfer, 1978; Blom-Zandstra, 1989). These nutrient imbalances also affect horticultural crop quality, as discussed above.

Many other factors influencing nutrient accumulation are related to nutrient transport and source-sink relations. For example, alterations in water economy affect calcium input. Since calcium is transported mainly in the transpiration stream (Grange and Hand, 1987), bagging fruit may result in lower calcium concentrations and higher calcium-related disorders (Witney et al., 1991; Hofman et al., 1997), due to increased relative humidity. Nevertheless, evidence is not conclusive (Saure, 2005). Canopy position and crop load also influence calcium input. Tree vigor is usually associated with lower calcium and magnesium content in fruits (Witney et al., 1990a,b). Fruit from upper parts of the canopy tend to show lower calcium contents (Ferguson and Triggs, 1990), and heavy cropping trees have fruit with higher calcium and lower potassium concentrations (Ferguson and Watkins, 1992). Nevertheless, calcium transport to fruit may be based on a hormonal control; gibberellins have been shown to inhibit calcium translocation (Saure, 2005).

Tree size, spacing, row orientation, canopy shape and training system influence light distribution within fruit trees, which in turn may affect mineral composition. In grapes, improvement of light penetration into the canopy enhanced anthocyanin and soluble phenol levels, but reduced potassium content (Prange and DeEll, 1997). In kiwifruit, light promoted calcium accumulation (Montanaro et al., 2006). The finding was not fully explained by fruit transpiration, a regulatory mechanism governed by phytohormones, which could play a role in determining calcium concentrations. Besides, the effect of sunlight does not seem to be universal: avocado fruit from the sunny side of trees did not contain significantly more calcium than fruit from the shaded side (Witney et al., 1990a).

The mineral content of some horticultural species seems to be affected under intensive culture systems (e.g. glasshouse) or organic conditions. Tomato fruit showed higher calcium and lower potassium, magnesium and sodium concentrations when grown on organic (compost/soil mix) versus hydroponic substrates (Premuzic et al., 1998). Smith (1993) reported higher mineral contents in organically cultivated apples, pears, potatoes and corn in comparison to conventionally cultivated ones. In contrast, Petersen and Pedersen (1991) did not find differences in mineral content between organically and conventionally cultivated vegetables. Hakala and co-workers (2003) reported that organic cultivation did not affect strawberry mineral contents consistently.

#### **Postharvest practices influencing mineral content of fruits and vegetables**

Postharvest treatments with minerals, primarily calcium, are used to improve the storage life and quality of different fruits and vegetables. In the last decade, the industry has been encouraged to fortify food and beverages with calcium. Increasing the calcium content of horticultural crops may give consumers new ways to enhance their calcium intake without resorting to supplements. In addition, the use of phosphorus-free sources of calcium can help to obtain a good balance of calcium and phosphorus in the diet (Martín-Diana et al., 2007).

Two major methods of postharvest application of calcium in horticultural crops are used: (1) dipping-washing and (2) impregnation processes (Martín-Diana et al., 2007). Dipping treatments are used for fresh, sensitive products, such as leafy vegetables. The delicate texture of berries prevents the use of vacuum infiltration, and dips in a solution of  $\text{CaCl}_2$  are used (García et al., 1996), followed by the removal of excess washing solution. On the other hand, impregnation modifies the composition of food material through partial water removal and impregnation of solutes, with no impairment of the material integrity. The process-driven forces can be osmotic gradient between the sample and solution, application of vacuum followed by atmospheric condition restoration, or both. Calcium chloride has been widely used as firming agent and preservative for both whole and fresh-cut fruits and vegetables, as discussed above.

### **C. Effect of minerals on fruit and vegetable quality and consumer acceptance**

Consumers buy certain items as good sources of specific minerals: potatoes and sweet potatoes for potassium, bananas for magnesium and potassium, spinach for iron, potassium, magnesium and as a non-dairy source of calcium. Mineral content of products is usually determined by ashing and atomic absorption (Pomeranz and Meloan, 1987). Without advanced analytical equipment, the consumer cannot detect differences in individual products at the point of purchase (Institute of Food Technologists, 1990). These attributes are considered credence attributes (see also Chapter 3), because they cannot be detected readily either by visual inspection or by consumption. Therefore, there is little or no incentive to measure mineral content in a quality control program, unless specific nutritional claims can be made.

Nevertheless, the consumer uses other criteria to judge quality. Quality attributes (see Chapter 3) include purchase attributes (i.e. size, color, firmness to the touch, aroma and absence of defects) and consumption attributes (i.e. flavor, mouth feel). Many of these quality characteristics are also affected by the mineral content and constitute part of a wider range of factors affecting fruit and vegetable acceptability. Acceptability, which is defined as “the level of continued purchase or consumption by a specific population” (Land, 1988), determines the consumption levels of many hidden essential nutrients: vitamins, antioxidants, fiber. Thus, the effect of minerals on horticultural crop quality attributes and consumer acceptance should be considered.

#### **Effect of minerals on color**

In apples and pears, both leaf and fruit nitrogen positively correlates with fruit green background color (Raese, 1977; Marsh et al., 1996), regardless of the rootstock used (Fallahi et al., 1985). Manganese has also been associated with green ground color in apples (Deckers et al., 1997). Excessive nitrogen application inhibits background color change from green to yellow and induces deficient reddish blush development and poor edible quality of peaches (Sistrunk, 1985; Crisosto et al., 1995; Crisosto et al., 1997). High nitrogen application also decreases fruit color in grapes (Kliewer, 1977). In *Citrus*, nitrogen is associated with an undesirable retardation of endogenous chlorophyll catabolism (Koo et al., 1974) and postharvest treatments with ethylene may be required to accelerate the loss of the green color (de-greening).

In apples, amelioration of potassium deficiencies can increase red fruit color, but such an effect is often not apparent when tree potassium status is adequate (Nielsen and Nielsen, 2003). In tomatoes, potassium deficiency is associated with lower levels of lycopene and higher levels of  $\beta$ -carotene (Trudel and Ozgun, 1971).

#### **Effect of minerals on flavor**

Nitrogen status negatively correlates with soluble solids, both in apples (Fallahi et al., 1985; Dris et al., 1999) and in pears (Raese, 1977). In contrast, soluble solid content increases with increasing fertilizer nitrogen levels in tomatoes (Barringer et al., 1999).

Apple calcium and phosphorus were both negatively correlated with fruit soluble solids at harvest, and after six months of 0°C storage, while fruit K/Ca ratio was positively correlated with titratable acidity (Fallahi et al., 1985). In mango, total soluble solids increased when zinc sulfate fertilizer was applied to the soil (Bahadur et al., 1998).

In “Fino 49” lemons, salinity reduces juice percentage and impairs juice quality by decreasing the total soluble solids and titratable acidity (García-Sánchez et al., 2003). Reduction of titratable acidity could be due to the greater accumulation of  $\text{Cl}^-$ , compared to  $\text{Na}^+$ , which could be compensated for by the degradation of organic acids for charge balance.

Minerals are also known to affect the production of several classes of volatile compounds in pome fruit (reviewed in Mattheis and Fellman, 1999). In fresh onions, increased sulfur availability enhances pungency and total sulfur flavor, but decreases the amounts of precursors for volatiles imparting “green” and “cabbage” notes (Randle, 1997).

**Effect of minerals on firmness**

Excess nitrogen fertilization can result in a decrease in firmness (Reeve, 1970; Prange and DeEll, 1997). Low phosphorus may also result in a loss of firmness in low-calcium content fruit (Sharples, 1980). The relationship between calcium and fruit firmness has been extensively studied and reviewed (Ferguson, 1984; Poovaiah et al., 1988; Harker et al., 1997; Sams, 1999). Higher firmness values and/or slower softening rates after harvest/storage have been associated with higher calcium concentrations, or with calcium applications in different fruit species, such as apples and pears (Fallahi et al., 1985; Raese and Drake, 1993, 2000a,b, 2002; Gerasopoulos and Richardson, 1999; Benavides et al., 2001); kiwifruit (Hopkirk et al., 1990; Gerasopoulos and Drogoudi, 2005); and strawberries (Chéour et al., 1990). Calcium foliar sprays on peaches and nectarines lead to a slight increase of calcium content (Manganaris et al., 2005a, 2006). Under Californian conditions, no consistent effect on fruit quality of mid- or late-season peach and nectarine varieties was found (reviewed in Crisosto et al., 1997).

Postharvest calcium treatments have been reported to retain fruit firmness in different horticultural products, among them, apples (Wang et al., 1993; Conway et al., 1994), peaches (Manganaris et al., 2005b, 2007), strawberries (Morris et al., 1985; García et al., 1996), lemons (Valero et al., 1998; Martínez-Romero et al., 1999), sliced pears and strawberries (Rosen and Kader, 1989). Calcium effects on fruit firmness are attributable to calcium's ability to cross-link with the pectic polysaccharide network by ionic association. Calcium binding may reduce the accessibility of cell wall degrading enzymes to their substrates.

**Effect of minerals on rots, physiological disorders and nutritional value**

In calcium-treated fruit, the association between firmness retention and reduced rot incidence suggests that calcium may affect both processes simultaneously through its cellular role in strengthening plant cell walls (García et al., 1996; Fallahi et al., 1997; Conway et al., 1999). On the other hand, high nitrogen fertilization increases susceptibility to decay caused by *Monilinia fructicola* (brown rot) in nectarines (Daane et al., 1995). Wounded and brown rot inoculated Fantasia and Flavortop nectarines from trees having more than 2.6% leaf nitrogen are more susceptible to *Monilinia fructicola* than fruit from trees with 2.6% or less leaf nitrogen (Michailides et al., 1993).

Consumers consider that fruits have less predictable eating quality than manufactured snacks. In fact, the effect of nutrients on the final quality of horticultural products may not become evident until harvest, distribution or consumption. The expression "latent damage" was coined by Peleg (1985) and later defined by Shewfelt (1986) as "damage incurred at one step but not apparent until a later step" to describe the result of non-visible quality loss. Physiological disorders may be a type of latent damage. Some physiological disorders relate to the imbalance between nutrients. Calcium is the nutrient most commonly associated with postharvest disorders. A calcium-deficient status is considered an important preharvest factor related to numerous physiological disorders of fruits and vegetables, such as bitter pit in pome fruit, blossom-end rot in tomato, blackheart in celery, cracking and cavity spot

in carrot and tip burn in lettuce and cabbage (reviewed in Ferguson et al., 1999), although some authors have questioned the role of calcium in these disorders (Saure, 1998, 2001). Other calcium-related disorders are associated with long-term cold storage, such as chilling injury in muskmelon (Combrink et al., 1995) and avocado (Chaplin and Scott, 1980). Postharvest calcium applications limited the incidence of chilling injury in peach fruit, expressed as flesh browning, after four weeks cold storage at 5°C (Manganaris et al., 2007). Nevertheless, preharvest calcium applications showed no effect on the onset of chilling injury in peaches and nectarines (reviewed in Lurie and Crisosto, 2005).

Magnesium and potassium have been considered as part of an index to predict bitter pit (Bramlage et al., 1985; Autio et al., 1986). Fallahi and Righetti (1984) proposed the relation between nitrogen and calcium as an important component of a diagnosis and recommendation system (DRIS) for apple. High rates of nitrogen application exacerbate the incidence of many physiological disorders, such as apricot pit burn (Bussi and Amiot, 1998, 2003).

In addition, minerals can influence the concentrations of other nutrients in horticultural crops. Nitrogen fertilizers at high rates tend to decrease the concentration of vitamin C in fruits (citrus juices) and vegetables (potatoes, cauliflower, white cabbage, crisphead lettuce, etc.) while increased potassium fertilization increases ascorbic acid content (reviewed in Lee and Kader, 2000).

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