Additives and Contaminants

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Introduction

For centuries, ingredients man has utilized food additives to improve and preserve foods. For centuries, we have used salt to preserve meats and fish, added herbs and spices to improve the flavor of foods, preserved fruit with sugar, and pickled vegetables like in a vinegar solution. Consumers now have the expectation of flavorful, nutritious, safe, convenient, colorful and affordable. Food additives and processing techniques help =deliver foods with these attributes. There is also a strong consumer desire for clean labels and foods without additives. This presents the food chemist with many conundrums about the use of additives.

There are thousands of ingredients approved for use in foods. The Food and Drug Administration (FDA) maintains a list of over 3000 ingredients in its data base "Everything Added to Food in the United States", many of which we use at home every day (e.g., sugar, baking soda, salt, vanilla, yeast, spices and colors) partially sliced loaf of bread.

All food additives are carefully regulated by federal authorities and various international organizations to ensure that foods are safe to eat and are accurately labeled.

In addition to ingredients that are added directly for benefits foods can contain toxic materials that are produced by the plant, animal, fungus or as a result of microbial contamination,

Food Toxins

In the 1500s Paracelsus expressed the classic toxicology maxim "All things are poison and nothing is without poison; only the dose makes a thing not a poison." This is often condensed to: "The dose makes the poison".

There is also the possibility of harmful or toxic substances entering the food supply unintentionally through direct contamination, through environmental pollution, as a result of processing or through deliberate adulteration for economic benefit. In addition, many foods can contain toxic materials. It should be kept in mind that most chemicals have a safe range of use but at very high doses can be toxic. Most compounds that we would consider in food have a dose response where they are inconsequential at low doses then can become toxic and very toxic. This can be seen with ingredients ranging from pesticides to common ingredients like salt. The concentration effects are very different but the typical dose response curve is similar for most chemicals or food ingredients. The key is to identify the safe level and typically we identify the "no adverse effect level" (NOAEL). This can be seen in Fig. 15.1.

The toxicity of some materials will differ greatly among individuals. There is a distribution what concentration of a material will affect individuals. There are variations in sensitivity to even the most common food ingredients. For example,

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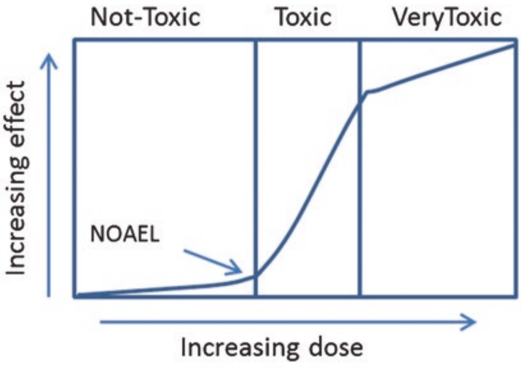


Fig. 15.1 Dose response curve for an ingredient or a drug illustrating the NOAEL

some populations are sensitive to salt while the bulk of the population is unaffected. Figure 15.2 illustrates the distribution in sensitivity to food, drugs or toxins for the same dose of a food ingredient or a drug.aflatoxin.

Many naturally occurring food compounds may be toxic as naturally-occurring constituent, microbial activity handling or processing, the incidence of adverse reactions from food is relatively low. The low incidence of adverse effects is the result solutions by the US Food and Drug Administration (FDA) and other regulatory agencies. The application of specifications, action levels, tolerances, warning labels and prohibitions have been effective in controlling the number of adverse events from food consumption. Regardless of preventative measures to protect consumers from natural food toxins, consumption of small levels of these materials is inevitable. The risk for toxicity due to consumption of food toxins is relatively low, however, there is always the possibility of toxicity due to contamination, overconsumption, allergy or an unpredictable idiosyncratic response.

Sources of food born toxins include certain sea foods, microbial contamination and production of mycotoxins and natural toxins present in plant fungal and sea foods. The increased use of dietary supplements by consumers also present sources of natural toxins. Table 15.1 contains a list of a few natural toxins found in the food supply. These materials cause a range of symptoms from gastrointestinal upset to death. These materials represent both toxins produced by the species and contaminants resulting from microbiological activity such as aflatoxins.

Fungal toxins, also called mycotoxins, are produced by fungi or molds. Most of the interest in fungal toxins is concerned with the so-called storage fungi, molds that grow on relatively dry cereals and oilseeds. These belong to two common genera, Aspergillus and Penicillium. The most common of the fungal toxins are the aflatoxins formed by members of the Aspergillus flavus group. The aflatoxins were discovered as a result of widespread poisoning of turkeys in the early 1960s in England through feeding of toxic peanut meal. The aflatoxins belong to the most powerful toxins known and are highly carcinogenic. A dose of 1 mg given to rats for short or long periods can result in liver cancer, and a diet containing 0.1 ppm of aflatoxin produces liver tumors in 50% of male rats (Spensley 1970). There are at least eight aflatoxins, of which the more important are designated B1, B2, G1, and G2. The names result from the blue and green fluorescence of these compounds when viewed under ultraviolet light. Aflatoxin B1 is a very powerful liver carcinogen; a level of 15 ppb in the diet of rats resulted in tumors in 100% of cases after 68 weeks (Scott 1969). Ducklings are used as test animals because they are especially sensitive to aflatoxins. The aflatoxins, for which the formulas are shown in Fig. 15.3, can occur in many foods but are particularly common in peanuts. Roasting of peanuts reduces the level of aflatoxin; for example, roasting for a half hour at 150° may reduce aflatoxin B1 content by as much as 80% (Scott 1969). However, aflatoxin may still be carried over into peanut butter. In addition, aflatoxins have been found in cottonseed meal, rice, sweet potatoes, beans, nuts, and wheat. Through ingestion of moldy feed by animals, aflatoxins may end up as contaminants in milk and meat. Aflatoxins found in milk may be M1 or M2, where M stands for metabolic; these are also toxic. The development of aflatoxins depends very much on temperature and moisture conditions. With peanuts, contamination occurs mostly during the drying period. Improper drying and storage are responsible for most of the

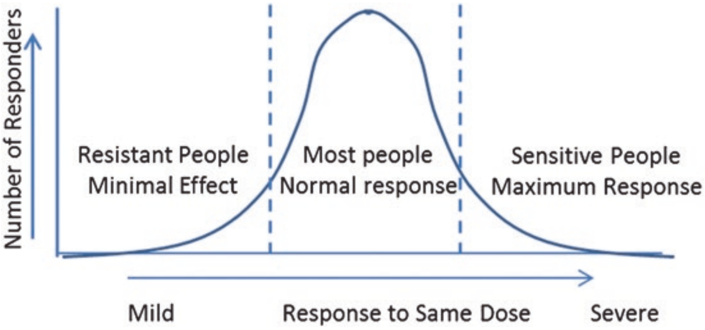


Fig. 15.2 Typical distribution of sensitivities to food ingredients or drugs in a population

Table 15.1 Natural toxins found in foods, their food source and effects when consumed

Toxic material	Food source	Effects
Ciguatoxin from Dinoflagellates (marine algae) in the genus Gambierdiscus	Consumption of subtropical and tropical marine finfish that have accumulated ciguatoxins through their diets	Combination of gastrointestinal, neurological, and, occasionally, cardiovascular disorders
Shellfish poisoning is caused by a group of toxins produced by planktonic algae consumed by shellfish	Paralytic shellfish poisoning(PSP)	PSP—can be deadly
	Diarrhetic shellfish poisoning(DSP)	DSP—nausea, vomiting, diarrhea
	Neurotoxic shellfish poisoning (NSP)	GI effects plus NSP-Neurological loss of short-term memory
	Amnesic shellfish poisoning(ASP)	(ASP) and AZP nausea, vomiting, diarrhea
	Azaspiracid shellfish poisoning(AZP)	
Scombrotoxin is a combination of substances, histamine prominent among them	Scombrotoxin is a combination of substances, histamine prominent among them. Histamine is produced during decomposition of fish	Tingling or burning in or around the mouth or throat, rash or hives, drop in blood pressure, headache, dizziness, itching of the skin, nausea, vomiting, diarrhea
Tetrodotoxin (TTX) and related compounds (e.g. 4,9-anhydroTTX, 4-epiTTX, 11-deoxyTTX, tetrodonic acid)	Pufferfish Multiple species Muscle is edible Toxin is in gonads (mainly ovary), liver, intestines, and skin can contain levels of tetrodotoxin sufficient to produce rapid death	Death is from respiratory-muscle paralysis and usually occurs within 4–6 h, with a known range of about 20 min to 8 h if victims survive the initial 24 h, they are expected to recover full
Mushroom toxins: Amanitin, Gyromitrin, Orellanine, Muscarine, Ibotenic Acid, Muscimol, Psilocybin, Coprine	Consumption of raw or cooked fruiting bodies (mushrooms, toadstools) of a number of species of higher fungi. T	Protoplasmic poisons—life-threatening poisons
		Neurotoxins—profuse sweating, coma, convulsions, hallucinations, excitement, depression, spastic colon
		Gastrointestinal irritants—transient nausea, vomiting, abdominal cramping, and diarrhea
Aflatoxins (AFs) are mycotoxins produced by certain fungi and can cause serious illness in animals and humans	Produced mainly by certain strains of Aspergillus flavus and A. parasiticus	Cancer, impaired protein formation, impaired blood coagulation, toxic hepatitis, AFB1 is the most potent known natural carcinogen and is the most abundant of the AFs
The four major aflatoxins are AFB1, AFB2, AFG1, and AFG2	Occur in a broad range of agricultural commodities, such as corn and nuts	
Pyrrolizidine alkaloids are a large class of naturally occurring alkaloids containing pyrrolizidine rings	Widely distributed in the plant kingdom, particularly in the Boraginaceae, Compositae, and Leguminosae families	pain, particularly in the right upper part of the abdomen; nausea; vomiting; swollen belly; swollen veins on the belly; puffiness from fluid; and fever
Phytohaemagglutinin (kidney bean lectin)	Red kidney bean (Phaseolus vulgaris) poisoning and kinkoti bean poisoning are examples of names for the illness caused by phytohaemagglutinin	Usually begins with extreme nausea and vomiting within 1–3 h of ingestion of the product, with diarrhea developing later

Compiled from: www.fda.gov/food/foodborneillnesscontaminants/causesofillnessbadbugbook/ucm2006773.htm

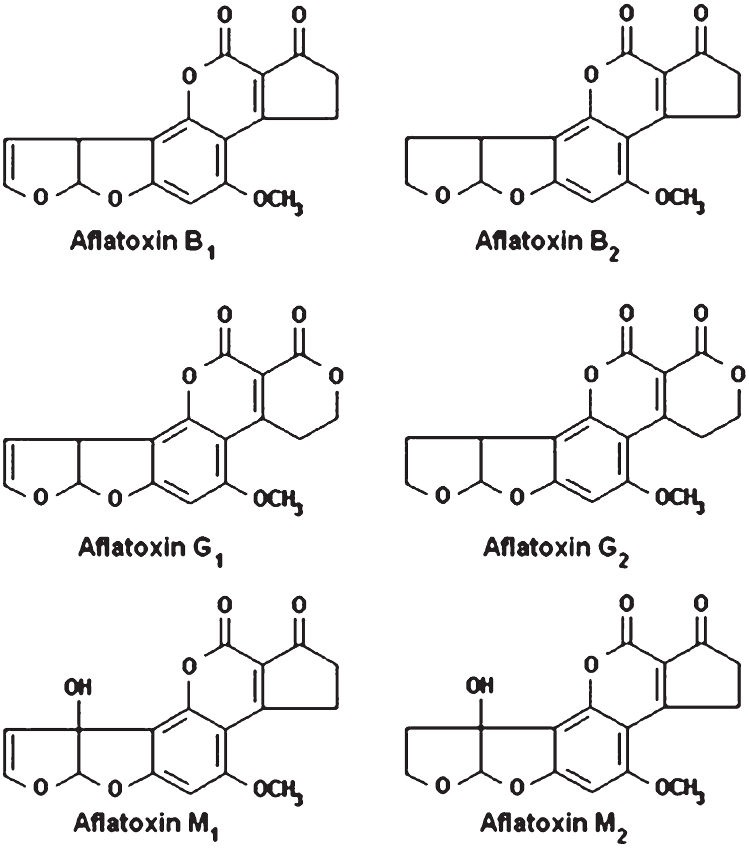


Fig. 15.3 Chemical structure of aflatoxins B_1, B_2, G_1, G_2, M_1 and M_2

contamination. This has been found to apply for rice. Optimum conditions for growth of Aspergillus flavus are 25° to 40 °C with a relative humidity greater than 85%.

Sterigmatocystin, which is a carcinogenic metabolite of Aspergillus ochraceus, has been found to be a natural contaminant of foods, especially com. Molds of the species Fusarium produce several mycotoxins in countries with moderate climates (Andrews et al. 1981). Two of these are zearalenone and deoxynivalenol (Fig. 15.4). Zearalenone, of F-2 toxin, is produced by Fusarium molds that grow on com (Marasas et al. 1979) that is immature or high in moisture at harvest. Deoxynivalenol, also known as vomitoxin, has been found in wheat and barley (Trenholm et al. 1981; Scott et al. 1983). During the wet summer of 1980, wheat grown in Ontario showed sprouting of kernels and pink discoloration. Experiments on milling showed that the vomitoxin was distributed throughout the milled products and was not destroyed by the bread-making process. Patulin is another Aspergillus metabolite and has been indicated as a food contaminant, especially in fruits, as a result of storage rot. It has been found as a constituent of apple juice (Harwig et al. 1973).

Control measures for prevention of aflatoxin production focus on reduction of water activity to a point where the fungus is unable to grow and maintenance of low water activity during storage. A moisture content of 18.0–19.5% in cereal grains is required for growth and toxin production by A. flavus. Aflatoxin-contaminated commodities can be detoxified by treatment with ammonia, calcium hydroxide, or a combination of formaldehyde and calcium hydroxide (Palmgren and Hayes 1987).

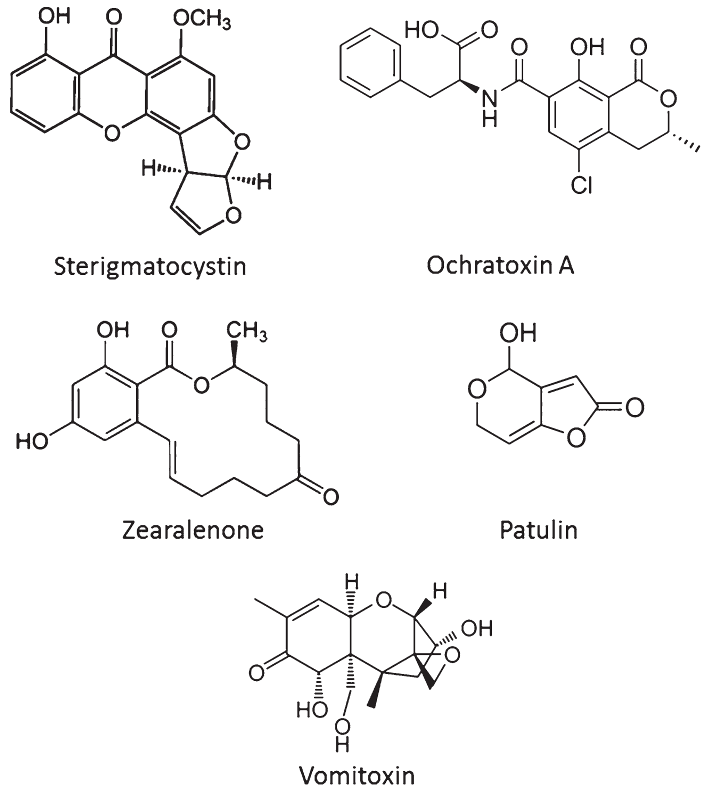


Fig. 15.4 Chemical structures of sterigmatocystin, ochratoxin A, zearalenone, deoxynivalenol (vomitoxin), and patulin

Food Additives

The term food additive means any substance the intended use of which results, or may reasonably be expected to result, directly or indirectly in its becoming a component or otherwise affecting the characteristics of any food (including any substance intended for use in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting, or holding food; and including any source of radiation intended for any such use), if such a substance is not generally recognized, among experts qualified by scientific training and experience to evaluate its safety, as having been adequately shown through scientific procedures (or, in the case of a substance used in food prior to January 1, 1958, through either scientific procedures or experience based on common use in food) to be safe under the condition of its intended use; except that such a term does not include pesticides, color additives and substances for which prior sanction or approval was granted.

Food additives can be divided into two major groups, intentional additives and incidental additives. Intentional additives are chemical substances that are added to food for specific purposes. All additives whether intentional, uunintentional or incidental additives are regulated by strict governmental controls. The U.S. law governing additives in foods is the Food Additives Amendment to the Federal Food, Drug and Cosmetic Act of 1958. According to this act, a food additive is defined as follows:

> Any substance that is reasonably expected to become a component of food is a food additive that is subject to premarket approval by FDA, unless the substance is generally recognized as safe (GRAS) among experts qualified by scientific training and experience to evaluate its safety under the conditions of its intended use, or meets one of the other exclusions from the food additive definition in section 201(s) of the Federal Food, Drug, and Cosmetic Act (FFDCA). Any food additive that is intended to have a technical effect in the food is deemed unsafe unless it either conforms to the terms of a regulation prescribing its use or to an exemption for investigational use. Otherwise, in accordance with section 409 of the Act, the substance is deemed an unsafe

> food additive. Any food that contains an unsafe food additive is adulterated under section 402(a)(2)(C) of the FFDCA.
>
> Similarly, any substance that is added to food and imparts color to the food is a color additive (see color additive definition in §201(t) of the FFDCA and 21 CFR 70.3(f)). Any color additive in food is deemed unsafe unless its use is either permitted by regulation or exempt by regulation. Unlike the definition for food additive, there is no GRAS exemption for color additives. Any food that contains an unsafe color additive is adulterated under section 402(c) of the FFDCA.
>
> The decision tree below will help in determining the regulatory status of a food ingredient. It is the responsibility of the manufacturer of any food to ensure that all ingredients used are of food-grade purity and comply with specifications and limitations in all applicable authorizations. The overall regulatory status of a food is affected by the regulatory status of each individual food ingredient. To determine compliance, consider each authorization to be composed of three parts:
>
> - The *identity* of the substance,
> - *Specifications* including purity and physical properties, and
> - *Limitations* on the conditions of use.
>
> To assure a customer that an ingredient that is being shipped to them is not adulterated or misbranded, the ingredient manufacturer may want to provide a letter of guaranty with the shipment (see 21 CFR 7.13 for suggested forms of guaranty).

Food additives perform a variety of useful functions in foods. Food ingredients that are intentionally introduced into foods to aid in processing, to act as preservatives, or to improve the quality of the food are called intentional additives. Food ingredients have been used for many years to preserve, flavor, blend, thicken and color foods, and have played an important role in reducing serious nutritional deficiencies among consumers. These ingredients also help ensure the availability of flavorful.

The FDA defines the utility of food additives as follows:

> To Maintain or Improve Safety and Freshness: Preservatives slow product spoilage caused by mold, air, bacteria, fungi or yeast. In addition to maintaining the quality of the food, they help control contamination that can cause foodborne illness, including life-threatening botulism. One group of preservatives—antioxidants—prevents fats and oils and the foods containing them from becoming rancid or developing an off-flavor. They also prevent cut fresh fruits such as apples from turning brown when exposed to air.
>
> To Improve or Maintain Nutritional Value: Vitamins and minerals (and fiber) are added to many foods to make up for those lacking in a person's diet or lost in processing, or to enhance the nutritional quality of a food. Such fortification and enrichment has helped reduce malnutrition in the U.S. and worldwide. All products containing added nutrients must be appropriately labeled.
>
> Improve Taste, Texture and Appearance: Spices, natural and artificial flavors, and sweeteners are added to enhance the taste of food. Food colors maintain or improve appearance. Emulsifiers, stabilizers and thickeners give foods the texture and consistency consumers expect. Leavening agents allow baked goods to rise during baking. Some additives help control the acidity and alkalinity of foods, while other ingredients help maintain the taste and appeal of foods with reduced fat content.

The use of food additives strictly regulated by national and international laws. The National Academy of Sciences (1973) has listed the purposes of food additives as follows:

- to improve or maintain nutritional value
- to enhance quality
- to reduce wastage
- to enhance consumer acceptability
- to improve keeping quality
- to make the food more readily available
- to facilitate preparation of the food

The use of food additives is in effect a food processing method, because both have the same objective—to preserve the food and/or make it more attractive. In many food processing techniques, the use of additives is an integral part of the method, as is smoking, heating, and fermenting. The National Academy of Sciences (1973) has listed the following situations in which additives should *not* be used:

- to disguise faulty or inferior processes
- to conceal damage, spoilage, or other inferiority
- to deceive the consumer

- if use entails substantial reduction in important nutrients
- if the desired effect can be obtained by economical, good manufacturing practices
- in amounts greater than the minimum necessary to achieve the desired effects

There are several ways of classifying intentional food additives. One such method lists the following three main types of additives:

1. complex substances such as proteins or starches that are extracted from other foods (for example, the use of caseinate in sausages and prepared meats)
2. naturally occurring, well-defined chemical compounds such as salt, phosphates, acetic acid, and ascorbic acid
3. substances produced by synthesis, which may or may not occur in nature, such as coal tar dyes, synthetic β-carotene, antioxidants, preservatives, and emulsifiers

Some of the more important groups of intentional food additives and their functions are described in Table 15.2.

Under the Food Additives Amendment, two groups of ingredients were exempted from the regulation process.

GROUP I—Prior-sanctioned substances—are substances that FDA or USDA had determined safe for use in food prior to the 1958 amendment. Examples are sodium nitrite and potassium nitrite used to preserve luncheon meats.

GROUP II—GRAS (generally recognized as safe) ingredients—are those that are generally recognized by experts as safe, based on their extensive history of use in food before 1958 or based on published scientific evidence. Among the several hundred GRAS substances are salt, sugar, spices, vitamins and monosodium glutamate (MSG). Manufacturers may also request that FDA review the industry's determination of GRAS Status (Hall 1975).

Preservatives or antimicrobial agents play an important role in today's supply of safe and stable foods. Increasing demand for convenience foods and reasonably long shelf life of processed foods make the use of chemical food preservatives imperative. Some of the commonly used preservatives—such as sulfites, nitrate, and salt—have been used for centuries in processed meats and wine. The choice of an antimicrobial agent has to be based on a knowledge of the antimicrobial spectrum of the preservative, the chemical and physical properties of both food and preservative, the conditions of storage and handling, and the assurance of a high initial quality of the food to be preserved (Davidson and Juneja 1990).

Benzoic Acid

Benzoic acid occurs naturally in many types of berries, plums, prunes, and some spices. As an additive, it is used as benzoic acid or as benzoate. The latter is used more often because benzoic acid is sparsely soluble in water (0.27% at 18 °C) and sodium benzoate is more soluble (66.0 g/100 mL at 20 °C). The undissociated form of benzoic acid is the most effective antimicrobial agent. With a pKa of 4.2, the optimum pH range is from 2.5 to 4.0. This makes it an effective antimicrobial agent in high-acid foods, fruit drinks, cider, carbonated beverages, and pickles. It is also used in margarines, salad dressings, soy sauce, and jams.

Parabens

Parabens are alkyl esters of p-hydroxybenzoic acid. The alkyl groups may be one of the following: methyl, ethyl, propyl, butyl, or heptyl. Parabens are colorless, tasteless, and odorless (except the methyl paraben). They are nonvolatile and nonhygroscopic. Their solubility in water depends on the nature of the alkyl group; the longer the alkyl chain length, the lower the solubility. They differ from benzoic acid in that they have antimicrobial activity in both acid and alkaline pH regions.

The antimicrobial activity of parabens is proportional to the chain length of the alkyl group. Parabens are more active against molds and

Table 15.2 Common food additives and their functions

Types of ingredients	Applications	Examples of uses	Products in foods
Preservatives	Prevent food spoilage from bacteria, molds, fungi, or yeast (antimicrobials); slow or prevent changes in color, flavor, or texture and delay rancidity (antioxidants); maintain freshness	Fruit sauces and jellies, beverages, baked goods, cured meats, oils and margarines, cereals, dressings, snack foods, fruits and vegetables	Ascorbic acid, citric acid, sodium benzoate, calcium propionate, sodium erythorbate, sodium nitrite, calcium sorbate, potassium sorbate, BHA, BHT, EDTA, tocopherols (Vitamin E)
Sweeteners	Add sweetness with or without the extra calories	Beverages, baked goods, confections, table-top sugar, substitutes, many processed foods	Sucrose (sugar), glucose, fructose, sorbitol, mannitol, corn syrup, high fructose corn syrup, saccharin, aspartame, sucralose, acesulfame potassium (acesulfame-K), neotame
Color additives	Offset color loss due to exposure to light, air, temperature extremes, moisture and storage conditions; correct natural variations in color; enhance colors that occur naturally; provide color to colorless and "fun" foods	Many processed foods, (candies, snack foods margarine, cheese, soft drinks, jams/jellies, gelatins, pudding and pie fillings)	FD&C Blue Nos. 1 and 2, FD&C Green No. 3, FD&C Red Nos. 3 and 40, FD&C Yellow Nos. 5 and 6, Orange B, Citrus Red No. 2, annatto extract, beta-carotene, grape skin extract, cochineal extract or carmine, paprika oleoresin, caramel color, fruit and vegetable juices, saffron (Note: Exempt color additives are not required to be declared by name on labels but may be declared simply as colorings or color added)
Flavors and spices	Add specific flavors (natural and synthetic)	Pudding and pie fillings, gelatin dessert mixes, cake mixes, salad dressings, candies, soft drinks, ice cream, BBQ sauce	Natural flavoring, artificial flavor, and spices
Flavor enhancers	Enhance flavors already present in foods (without providing their own separate flavor)	Many processed foods	Monosodium glutamate (MSG), hydrolyzed soy protein, autolyzed yeast extract, disodium guanylate or inosinate
Fat replacers (and components of formulations used to replace fats)	Provide expected texture and a creamy "mouth-feel" in reduced-fat foods	Baked goods, dressings, frozen desserts, confections, cake and dessert mixes, dairy products	Olestra, cellulose gel, carrageenan, polydextrose, modified food starch, microparticulated egg white protein, guar gum, xanthan gum, whey protein concentrate
Nutrients	Replace vitamins and minerals lost in processing (enrichment), add nutrients that may be lacking in the diet (fortification)	Flour, breads, cereals, rice, macaroni, margarine, salt, milk, fruit beverages, energy bars, instant breakfast drinks	Thiamine hydrochloride, riboflavin (Vitamin B_2), niacin, niacinamide, folate or folic acid, beta carotene, potassium iodide, iron or ferrous sulfate, alpha tocopherols, ascorbic acid, Vitamin D, amino acids (L-tryptophan, L-lysine, L-leucine, L-methionine)

Emulsifiers	Allow smooth mixing of ingredients, prevent separation	Salad dressings, peanut butter, chocolate, margarine, frozen desserts	Soy lecithin, mono- and diglycerides, egg yolks, polysorbates, sorbitan monostearate
	Keep emulsified products stable, reduce stickiness, control crystallization, keep ingredients dispersed, and to help products dissolve more easily		
Stabilizers and thickeners, binders, texturizers	Produce uniform texture, improve “mouth-feel”	Frozen desserts, dairy products, cakes, pudding and gelatin mixes, dressings, jams and jellies, sauces	Gelatin, pectin, guar gum, carrageenan, xanthan gum, whey
pH control agents and acidulants	Control acidity and alkalinity, prevent spoilage	Beverages, frozen desserts, chocolate, low acid canned foods, baking powder	Lactic acid, citric acid, ammonium hydroxide, sodium carbonate
Leavening agents	Promote rising of baked goods	Breads and other baked goods	Baking soda, monocalcium phosphate, calcium carbonate
Anti-caking agents	Keep powdered foods free-flowing, prevent moisture absorption	Salt, baking powder, confectioner’s sugar	Calcium silicate, iron ammonium citrate, silicon dioxide
Humectants	Retain moisture	Shredded coconut, marshmallows, soft candies, confections	Glycerin, sorbitol
Yeast nutrients	Promote growth of yeast	Breads and other baked goods	Calcium sulfate, ammonium phosphate
Dough strengtheners and conditioners	Produce more stable dough	Breads and other baked goods	Ammonium sulfate, azodicarbonamide, L-cysteine
Firming agents	Maintain crispness and firmness	Processed fruits and vegetables	Calcium chloride, calcium lactate
Enzyme preparations	Modify proteins, polysaccharides and fats	Cheese, dairy products, meat	Enzymes, lactase, papain, rennet, chymosin
Gases	Serve as propellant, aerate, or create carbonation	Oil cooking spray, whipped cream, carbonated beverages	Carbon dioxide, nitrous oxide

Adapted from: http://www.fda.gov/Food/IngredientsPackagingLabeling/FoodAdditivesIngredients/ucm094211.htm#types accessed 8/4/2016 yeasts than against bacteria, and more active against gram-positive than gram negative bacteria. They are used in fruitcakes, pastries, and fruit fillings. Methyl and propyl parabens can be used in soft drinks. Combinations of several parabens are often used in applications such as fish products, flavor extracts, and salad dressings.

Sorbic Acid

Sorbic acid is a straight-chain, *trans-trans* unsaturated fatty acid, 2,4-hexadienoic acid. As an acid, it has low solubility (0.15 g/100 mL) in water at room temperature. The salts, sodium, or potassium are more soluble in water. Sorbates are stable in the dry form; they are unstable in aqueous solutions because they decompose through oxidation. The rate of oxidation is increased at low pH, by increased temperature, and by light exposure.

Sorbic acid and sorbates are effective against yeasts and molds. Sorbates inhibit yeast growth in a variety of foods including wine, fruit juice, dried fruit, cottage cheese, meat, and fish products. Sorbates are most effective in products of low pH including salad dressings, tomato products, carbonated beverages, and a variety of other foods.

The effective level of sorbates in foods is in the range of 0.5–0.30%. Some of the common applications are shown in Table 15.3. Sorbates are generally used in sweetened wines or wines that contain residual sugars to prevent refermentation. At the levels generally used, sorbates do not affect food flavor. However, when used at higher levels, they may be detected by some people as an unpleasant flavor. Sorbate can be degraded by certain microorganisms to produce off-flavors. Molds can metabolize sorbate to produce 1,3 pentadiene, a volatile compound with an odor like kerosene. High levels of microorganisms can result in the degradation of sorbate in wine and result in the off-flavor known as geranium off-odor (Edinger and Splittstoesser 1986). The compounds responsible for the flavor defect are ethyl sorbate, 4-hexenoic acid, 1-ethoxyhexa-2,4-diene, and 2-ethoxyhexa-3,5-diene. The same problem may occur in fermented vegetables treated with sorbate.

Table 15.3 Applications of sorbates as antimicrobial agents

Products	Levels (%)
Dairy products: aged cheeses, processed cheeses, cottage cheese, cheese spreads, cheese dips, sour cream, yogurt	0.05–0.30
Bakery products: cakes, cake mixes, pies, fillings, mixes, icings, fudges, toppings, doughnuts	0.03–0.30
Vegetable products: fermented vegetables, pickles, olives, relishes, fresh salads	0.02–0.20
Fruit products: dried fruit, jams, jellies, juices, fruit salads, syrups, purees, concentrates	0.02–0.25
Beverages: still wines, carbonated and noncarbonated beverages, fruit drinks, low-calorie drinks	0.02–0.10
Food emulsions: mayonnaise, margarine, salad dressings	0.05–0.10
Meat and fish products: smoked and salted fish, dry sausages	0.05–0.30
Miscellaneous: dry sausage casings, semimoist pet foods, confectionery	0.05–0.30

Source: Reprinted with permission from J.N. Sofos and F.F. Busta, Sorbic Acid and Sorbates, in *Antimicrobials in Foods,* RM. Davidson and A.L. Branen, eds., p. 62, 1993, by courtesy of Marcel Dekker, Inc.

Table 15.4 Sources of SO_2 and their content of active SO_2

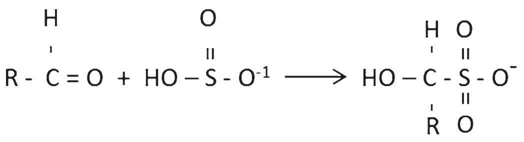
Chemical	Formula	Content of active SO_2 (%)
Sulfur dioxide	SO_2	100.00
Sodium sulfite, anhydrous	Na_2SO_3	50.82
Sodium sulfite, heptahydrate	$Na_2SO_3 \cdot 7H_2O$	25.41
Sodium hydrogen sulfite	$NaHSO_3$	61.56
Sodium metabisulfite	$Na_2S_2O_5$	67.39
Potassium metabisulfite	$K_2S_2O_5$	57.63
Calcium sulfite	$CaSO_3$	64.00

Sulfites

Sulfur dioxide and sulfites have long been used as preservatives, serving both as antimicrobial substance and as antioxidant. Their use as preservatives in wine dates back to Roman times. Sulfur dioxide is a gas that can be used in compressed form in cylinders. It is liquid under pressure of 3.4 atm and can be injected directly in liquids. It can also be used to prepare solutions in ice cold water. It dissolves to form sulfurous acid. Instead of sulfur dioxide solutions, a number of sulfites can be used (Table 15.4) because, when dissolved in water, they all yield active SO_2. The most widely used of these sulfites is potassium metabisulfite. In practice, a value of 50% of active SO_2 is used. When sulfur dioxide is dissolved in water, the following ions are formed:

$$SO_2\,(gas) \rightarrow SO_2\,(aq)$$
$$SO_2\,(aq)^+ \rightarrow H_2O \rightarrow H_2SO_3$$
$$H_2SO_3 \rightarrow H^+ + HSO_3^-\left(K_1 = 1.7\times10^{-2}\right)$$
$$HSO_3^- \rightarrow H^+ + SO_3^{2-}\left(K_2 = 5\times10^{-6}\right)$$
$$2HSO_3^- \rightarrow S_2O_5^{2-} + H_2O$$

All of these forms of sulfur are known as free sulfur dioxide. The bisulfite ion (HSO_3^-) can react with aldehydes, dextrins, pectic substances, proteins, ketones, and certain sugars to form addition compounds.



$$\mathrm{R-\overset{H}{\overset{|}{C}}=O + HO-\overset{O}{\overset{\|}{S}}-O^{-1} \longrightarrow HO-\underset{\underset{R}{|}}{\overset{H}{\overset{|}{C}}}-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-O^{-}}$$

The addition compounds are known as bound sulfur dioxide. Sulfur dioxide is used extensively in wine making, and in wine acetaldehyde reacts preferentially with bisulfite. Excess bisulfite reacts with sugars. It is possible to classify bound SO_2 into three forms: aldehyde sulfurous acid, glucose sulfurous acid, and rest sulfurous acid. The latter holds the SO_2 in a less tightly bound form. Sulfites in wines serve a dual purpose: (1) antiseptic or bacteriostatic and (2) antioxidant. These activities are dependent on the form of SO_2 present. The various forms of SO_2 in wine are represented schematically in Fig. 15.5. The free SO_2 includes the water-soluble SO_2 and the undissociated H_2SO_3 and constitutes about 2.8% of the total. The bisulfite form constitutes 96.3% and the sulfite form 0.9% (all at pH 3.3 and 20 °C). The bound SO_2 is mostly (80%) present as acetaldehyde SO_2, 1% as glucose SO_2, and 10–20% as rest SO_2. The various forms of sulfite have different activities. The two free forms are the only ones with antiseptic activity. The antioxidant activity is limited to the SO_3^{2-} ion (Fig. 15.5).

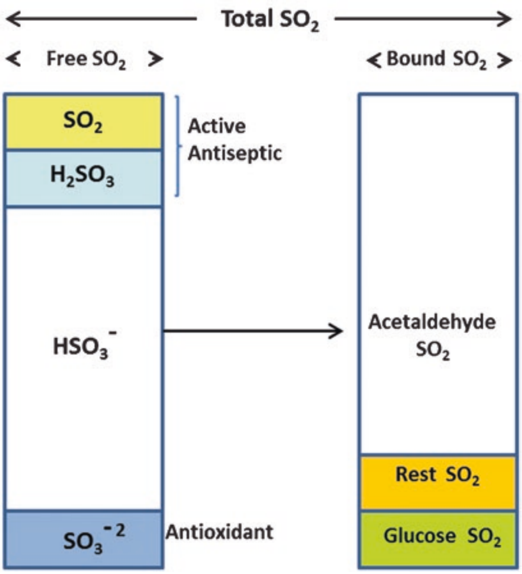


Fig. 15.5 The various forms of SO_2 in wine and their activity

Table 15.5 Effect of pH on the proportion of active antiseptic SO_2 of wine containing 100 mg/L free SO_2

pH	Active SO_2 (mg/L)
2.2	37.0
2.8	8.0
3.0	5.0
3.3	3.0
3.5	1.8
3.7	1.2
4.0	0.8

The antiseptic activity of SO_2 is highly dependent on the pH, as indicated in Table 15.5. The lower the pH, the greater the antiseptic action of SO_2. The effect of pH on the various forms of sulfur dioxide is shown in Fig. 15.6.

Sulfurous acid inhibits molds and bacteria and to a lesser extent yeasts. For this reason, SO2 can be used to control undesirable bacteria and wild yeast in fermentations without affecting the SO_2-tolerant cultured yeasts. According to Chichester and Tanner (1968), the undissociated acid is 1000 times more active than HSO_3—for Escherichia coli, 100–500 times for Saccharomyces cerevisiae, and 100 times for Aspergillus niger.

The amount of SO_2 added to foods is self-limiting because at levels from 200 to 500 ppm

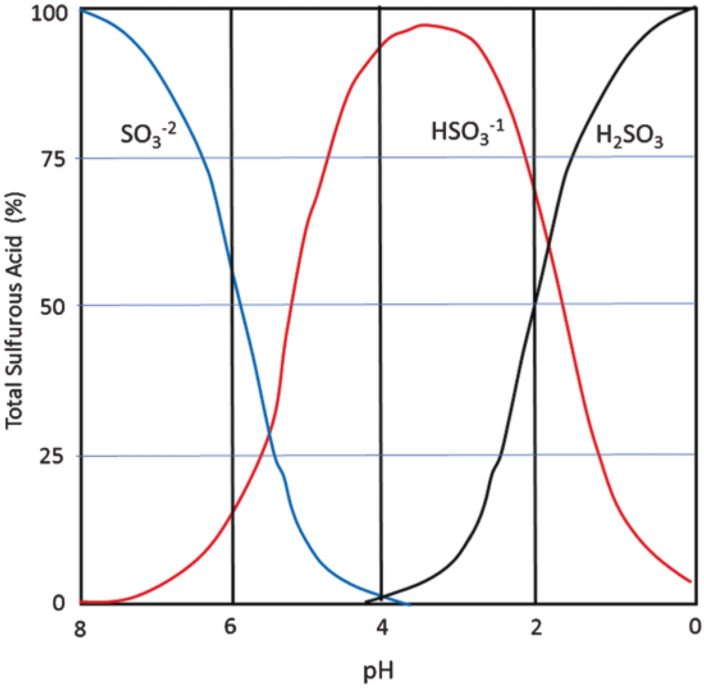


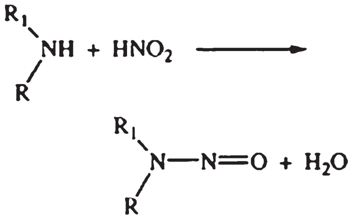
Fig. 15.6 Effect of pH on the ionization of sulfurous acid in water

the product may develop an unpleasant off-flavor. The acceptable daily intake (ADI) is set at 1.5 mg/kg body weight. Because large intakes can result from consumption of wine, there have been many studies on reducing the use of SO_2 in wine making. Although some other compounds (such as sorbic acid and ascorbic acid) may partially replace SO_2, there is no satisfactory replacement for SO_2 in wine making.

The use of SO_2 is not permitted in foods that contain significant quantities of thiamine, because this vitamin is destroyed by SO_2. In the United States, the maximum permitted level of SO_2 in wine is 350 ppm. Modern practices have resulted in much lower levels of SO_2. In some countries SO_2 is used in meat products; such use is not permitted in North America on the grounds that this would result in consumer deception. SO_2 is also widely used in dried fruits, where levels may be up to 2000 ppm. Other applications are in dried vegetables and dried potato products. Because SO_2 is volatile and easily lost to the atmosphere, the residual levels may be much lower than the amounts originally applied.

Nitrates and Nitrites

Curing salts, which produce the characteristic color and flavor of products such as bacon and ham, have been used throughout history. Curing salts have traditionally contained nitrate and nitrite; the discovery that nitrite was the active compound was made in about 1890. Currently, nitrate is not considered to be an essential component in curing mixtures; it is sometimes suggested that nitrate may be transformed into nitrite, thus forming a reservoir for the production of nitrite. Both nitrates and nitrites are thought to have antimicrobial action. Nitrate is used in the production of Gouda cheese to prevent gas formation by butyric acid–forming bacteria. The action of nitrite in meat curing is considered to involve inhibition of toxin formation by *Clostridium botulinum*, an important factor in establishing safety of cured meat products. Major concern about the use of nitrite was generated by the realization that secondary amines in foods may react to form nitrosamines, as follows:



The nitrosamines are powerful carcinogens, and they may be mutagenic and teratogenic as well. It appears that very small amounts of nitrosamines can be formed in certain cured meat products. These levels are in the ppm or the ppb range and, because analytical procedures are difficult, there is as yet no clear picture of the occurrence of nitrosamines. The nitrosamines may be either volatile or nonvolatile, and only the latter are usually included in analysis of foods. Nitrosamines, especially dimethyl-nitrosamine, have been found in a number of cases when cured meats were surveyed at concentrations of a few μg/kg (ppb). Nitrosamines are usually present in foods as the result of processing methods that promote their formation (Havery and Fazio 1985). An example is the spray drying of milk. Suitable modifications of these process conditions can drastically reduce the nitrosamine levels. Considerable further research is necessary to establish why nitrosamines are present only in some samples and what the toxicological importance of nitrosamines is at these levels. There appears to be no suitable replacement for nitrite in the production of cured meats such as ham and bacon. The ADI of nitrite has been set at 60 mg per person per day. It is estimated that the daily intake per person in Canada is about 10 mg.

Cassens (1997) has reported a dramatic decline in the residual nitrite levels in cured meat products in the United States. The current residual nitrite content of cured meat products is about 10 ppm. In 1975 an average residual nitrite content in cured meats was reported as 52.5 ppm. This reduction of nitrite levels by about 80% has been attributed to lower ingoing nitrite, increased use of ascorbates, improved process control, and altered formulations.

The nitrate-nitrite intake from natural sources is much higher than that from processed foods. Fassett (1977) estimated that the nitrate intake from 100 g of processed meat might be 50 mg and from 100 g of high-nitrate spinach, 200 mg. Wagner and Tannenbaum (1985) reported that nitrate in cured meats is insignificant compared to nitrite produced endogenously. Nitrate is produced in the body and recirculated to the oral cavity, where it is reduced to nitrite by bacterial action.

Hydrogen Peroxide

Hydrogen peroxide is a strong oxidizing agent and is also useful as a bleaching agent. It is used for the bleaching of crude soya lecithin. The antimicrobial action of hydrogen peroxide is used for the preservation of cheese milk. Hydrogen peroxide decomposes slowly into water and oxygen; this process is accelerated by increased temperature and the presence of catalysts such as catalase, lacto-peroxidase and heavy metals. Its antimicrobial action increases with temperature. When hydrogen peroxide is used for cheese making, the milk is treated with 0.02% hydrogen peroxide followed by catalase to remove the hydrogen peroxide. Hydrogen peroxide can be used for sterilizing food processing equipment and for sterilizing packaging material used in aseptic food packaging systems.

Sodium Chloride

Sodium chloride has been used for centuries to prevent spoilage of foods. Fish, meats, and vegetables have been preserved with salt. Today, salt is used mainly in combination with other processing methods. The antimicrobial activity of salt is related to its ability to reduce the water activity (a_w,), thereby influencing microbial growth. Salt has the following characteristics: it produces an osmotic effect, it limits oxygen solubility, it changes pH, sodium and chloride ions are toxic, and salt contributes to loss of magnesium ions (Banwart 1979). The use of sodium chloride is self-limiting because of its effect on taste.

Bacteriocins

Nisin is an antibacterial polypeptide produced by some strains of *Lactococcus lactis.* Nisin-like substances are widely produced by lactic acid bacteria. These inhibitory substances are known as bacteriocins. Nisin has been called an antibiotic, but this term is avoided because nisin is not used for therapeutic purposes in humans or animals. Nisin-producing organisms occur naturally in milk. Nisin can be used as a processing aid against gram-positive organisms. Because its effectiveness decreases as the bacterial load increases, it is unlikely to be used to cover up unhygienic practices.

Nisin is a polypeptide with a molecular weight of 3500, which is present as a dimer of molecular weight 7000. It contains some unusual sulfur amino acids, lanthionine and β-methyl lanthionine. It contains no aromatic amino acids and is stable to heat.

The use of nisin as a food preservative has been approved in many countries. It has been used effectively in preservation of processed cheese. It is also used in the heat treatment of nonacid foods and in extending the shelf life of sterilized milk.

A related antibacterial substance is natamycin, identical to pimaricin. Natamycin is effective in controlling the growth of fungi but has no effect on bacteria or viruses. In fermentation industries, natamycin can be used to control mold or yeast growth. It has a low solubility and therefore can be used as a surface treatment on foods. Natamycin is used in the production of many varieties of cheese.

Acids

Acids as food additives serve a dual purpose, as acidulante and as preservatives. Phosphoric acid is used in cola soft drinks to reduce the pH. Acetic acid is used to provide tartness in mayonnaise and salad dressings. A similar function in a variety of other foods is served by organic acids such as citric, tartaric, malic, lactic, succinic, adipic, and fumarie acid. The properties of some of the common food acids are listed in Table 15.6 (Peterson and Johnson 1978). Members of the straight-chain carboxylic acids, propionic and sorbic acids, are used for their antimicrobial properties. Propionic acid is mainly used for its antifungal properties. Propionic acid applied as a 10% solution to the surface of cheese and butter retards the growth of molds. The fungistatic effect is higher at pH 4 than at pH 5. A 5% solution of calcium propionate acidified with lactic acid to pH 5.5 is as effective as a 10% unacidified solution of propionic acid. The sodium salts of propionic acid also have antimicrobial properties.

Antioxidants

Food antioxidants in the broadest sense are all of the substances that have some effect on preventing or retarding oxidative deterioration in foods. They can be classified into a number of groups (Kochhar and Rossell 1990).

Primary antioxidants terminate free radical chains and function as electron donors. They include the phenolic antioxidants, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tertiary butyl hydroquinone (TBHQ), alkylgalates, usually propylgallate (PG), and natural and synthetic tocopherols and tocotrienols.

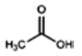
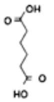
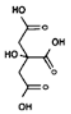
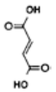
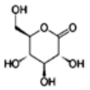
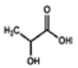
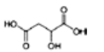
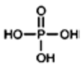
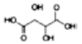
Oxygen scavengers can remove oxygen in a closed system. The most widely used compounds are vitamin C and related substances, ascorbyl palmitate, and erythorbic acid (the D-isomer of ascorbic acid).

Chelating agents or sequestrante remove metallic ions, especially copper and iron, that are powerful prooxidants. Citric acid is widely used for this purpose. Amino acids and ethylene diamine tetraacetic acid (EDTA) are other examples of chelating agents.

Enzymic antioxidants can remove dissolved or head space oxygen, such as glucose oxidase. Superoxide dismutase can be used to remove highly oxidative compounds from food systems.

Natural antioxidants are present in many spices and herbs (Lacroix et al. 1997; Six 1994). Rosemary and sage are the most potent antioxidant spices (Schuler 1990). The active principles in rosemary are carnosic acid and camosol (Fig. 15.7). Antioxidants from spices can be

Table 15.6 Properties of some common food acids

Property	Acetic acid	*Adipic acid*	Citric acid	Fumaric acid	Glucono-Delta lactone	lactic acid	Malic acid	Phos-phoric acid	Tartaric acid
									
Empirical formula	$C_2H_4O_2$	$C_6H_{10}O_4$	$C_6H_8O_7$	$C_4H_4O_4$	$C_6H_{10}O_6$	$C_3H_6O_3$	$C_4H_6O_5$	H_3PO_4	$C_4H_6O_6$
Physical form	Oily Liquid	Crystalline	Crystalline	Crystalline	Crystalline	85% Water Solution	Crystalline	85% Water Solution	Crystalline
Molecular weight	60.05	146.14	192.12	116.07	178.14	90.08	134.09	82.00	150.09
Equivalent weight	60.05	73.07	64.04	58.04	178.14	90.08	67.05	27.33	75.05
Physical form	Oily Liquid	Crystal-line	Crystal-line	Crystal-line	Crystal-line	85% Water	Crystal-line	85% Water Solution	Crystal-line
Molecular weight	60.05	146.14	192.12	116.07	178.14	90.08	134.09	82.00	150.09
Equivalentweight	60.05	73.05	64.04	58.04	178.14	90.08	67.05	27.03	75.05
Sol. in water (g/100 ml)	∞	1.4	181.00	0.63	59.0	∞	144.0	∞	147.0
K1	8×10^{-5}	3.7×10^{-5}	8.2×10^{-4}	1×10^{-3}	2.5×10^{-4} (gluconic acid)	1.37×10^{-4}	4×10^{-4}	7.25×10^{-3}	1.04×10^{-3}
K2		2.4×10^{-6}	1.77×10^{-5}	3×10^{-5}			9×10^{-6}	6.23×10^{-8}	5.55×10^{-3}
K3			3.9×10^{-6}					3×10^{-13}	

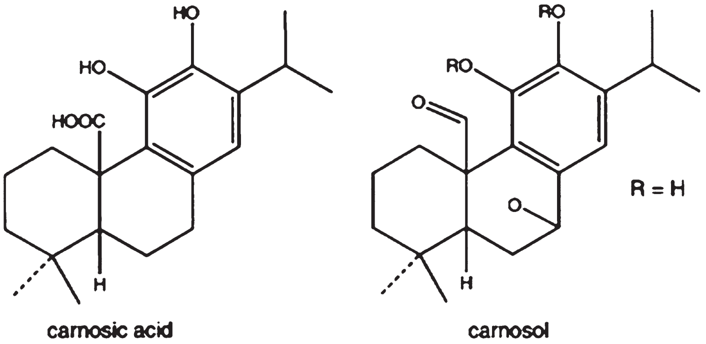


Fig. 15.7 Chemical structure of the active antioxidant principles in rosemary

obtained as extracts or in powdered form by a process described by Bracco et al. (1981).

The level of phenolic antioxidants permitted for use in foods is limited. U.S. regulations allow maximum levels of 0.02% based on the fat content of the food.

Sometimes the antioxidants are incorporated in the packaging materials rather than in the food itself. In this case, a larger number of antioxidants is permitted, provided that no more than 50 ppm of the antioxidants become a component of the food.

Emulsifiers

With the exception of lecithin, all emulsifiers used in foods are synthetic. They are characterized as ionic or nonionic and by their hydrophile/lipophile balance (HLB). All of the synthetic emulsifiers are derivatives of fatty acids.

Lecithin is the commercial name of a mixture of phospholipids obtained as a byproduct of the refining of soybean oil. Phosphatidylcholine is also known as lecithin, but the commercial product of that name contains several phospholipids including phosphatidylcholine. Crude soybean lecithin is dark in color and can be bleached with hydrogen peroxide or benzoyl peroxide. Lecithin can be hydroxylated by treatment with hydrogen peroxide and lactic or acetic acid. Hydroxylated lecithin is more hydrophilic, and this makes for a better oil-in-water emulsifier. The phospholipids contained in lecithin are insoluble in acetone.

Monoglycerides are produced by transesterification of glycerol with triglycerides. The reaction proceeds at high temperature, under vacuum and in the presence of an alkaline catalyst. The reaction mixture, after removal of excess glycerol, is known as commercial monoglyceride, a mixture of about 40% monoglyceride and di- and triglycerides. The di- and triglycerides have no emulsifying properties. Molecular distillation can increase the monoglyceride content to well over 90%. The emulsifying properties, especially HLB, are determined by the chain length and unsaturation of the fatty acid chain.

Hydroxycarboxylic and fatty acid esters are produced by esterifying organic acids to monoglycerides. This increases their hydrophilic properties. Organic acids used are acetic, citric, fumarie, lactic, succinic, or tartaric acid. Succinylated monoglycerides are synthesized from distilled monoglycerides and succinic anhydride. They are used as dough conditioners and crumb softeners (Krog 1981). Acetic acid esters can be produced from mono- and diglycerides by reaction with acetic anhydride or by transesterification. They are used to improve aeration in foods high in fat content and to control fat crystallization. Other esters may be prepared: citric, diacetyl tartaric, and lactic acid. A product containing two molecules of lactic acid per emulsifier molecule, known as stearoyl-2-lactylate, is available as the sodium or calcium salt. It is used in bakery products.

Polyglycerol esters of fatty acids are produced by reacting polymerized glycerol with edible fats. The degree of polymerization of the glycerol and the nature of the fat provide a wide range of emulsifiers with different HLB values.

Polyethylene or propylene glycol esters of fatty acids are more hydrophilic than monoglycerides. They can be produced in a range of compositions.

Sorbitan fatty acid esters are produced by polymerization of ethylene oxide to sorbitan fatty acid esters. The resulting polyoxyethylene sorbitan esters are nonionic hydrophilic emulsifiers. They are used in bakery products as antistaling agents. They are known as polysorbates with a number as indication of the type of fatty acid used (e.g., lauric, stearic, or oleic acid).

Sucrose fatty acid esters can be produced by esterification of fatty acids with sucrose, usually in a solvent system. The HLB varies, depending on the number of fatty acids esterified to a sucrose molecule. Monoesters have an HLB value greater than 16, triesters less than 1. When the level of esterification increases to over five molecules of fatty acid, the emulsifying property is lost. At high levels of esterification the material can be used as a fat replacer because it is not absorbed or digested and therefore yields no calories.

Bread Improvers

To speed up the aging process of wheat flour, bleaching and maturing agents are used. Benzoyl peroxide is a bleaching agent that is frequently used; other compounds—including the oxides of nitrogen, chlorine dioxide, nitrosyl chloride, and chlorine—are both bleaching and improving (or maturing) agents. Improvers used to ensure that dough will ferment uniformly and vigorously include oxidizing agents such as potassium bromate, potassium iodate, and calcium peroxide. In addition to these agents, there may be small amounts of other inorganic compounds in bread improvers, including ammonium chloride, ammonium sulfate, calcium sulfate, and ammonium and calcium phosphates. Most of these bread improvers can only be used in small quantities, because excessive amounts reduce quality. Several compounds used as bread improvers are actually emulsifiers and are covered under that heading.

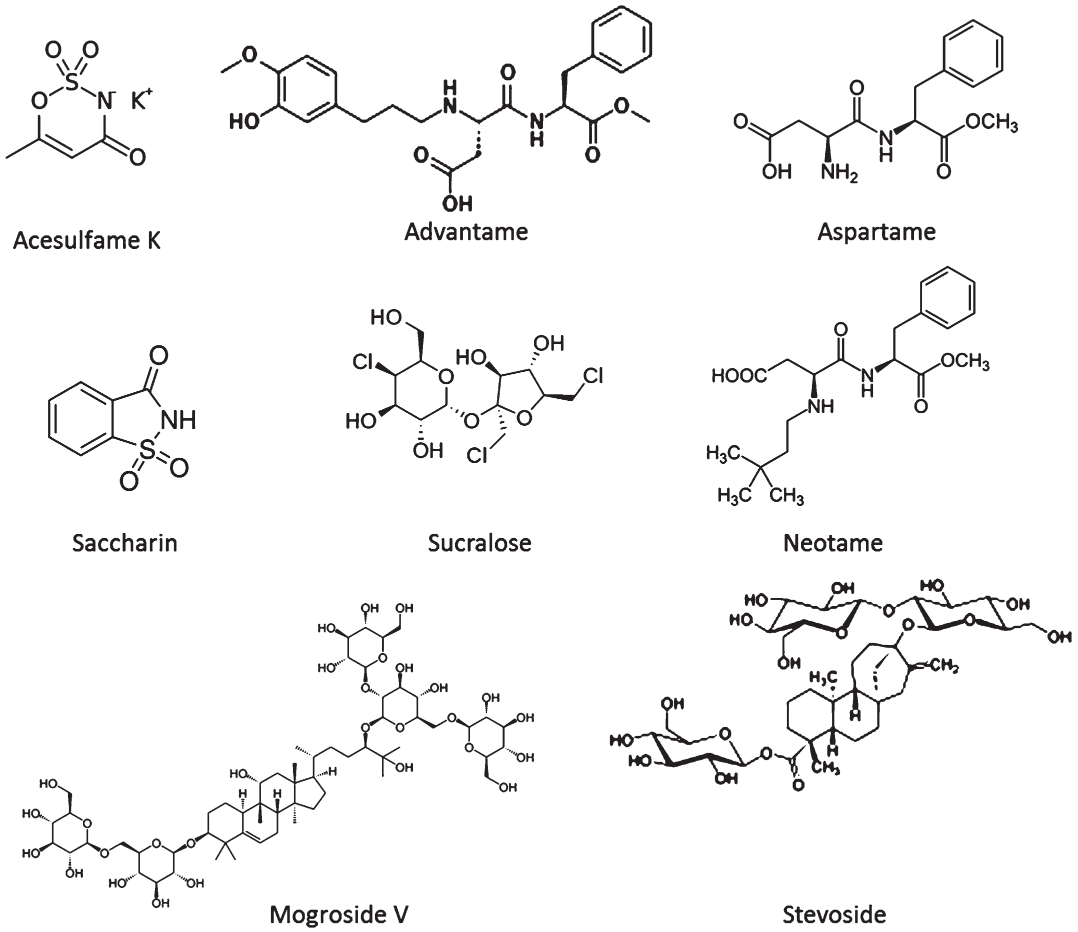
Sweeteners

Sweeteners can be divided into two groups, nonnutritive and nutritive sweeteners. The nonnutritive sweeteners include saccharin, cyclamate, aspartame, acesulfame K, and sucralose. Plant extracts from Stevia and Monk Fruit extract where the main sweetener is Mogroside V are plant extracts that have been approved for food uses. The nutritive sweeteners are sucrose; glucose; fructose; invert sugar; and a variety of polyols including sorbitol, mannitol, maltitol, lactitol, xylitol, and hydrogenated glucose syrups are discussed in Chap. 2.

The chemical structure of the most important nonnutritive sweeteners is shown in Fig. 15.8. Saccharin is available as the sodium or calcium salt of orthobenzosulfimide. The cyclamates are the sodium or calcium salts of cyclohexane sulfamic acid or the acid itself. Cyclamate is 30–40 times sweeter than sucrose, and about 300 times sweeter than saccharin. Organoleptic comparison of sweetness indicates that the medium in which the sweetener is tasted may affect the results. There is also a concentration effect. At higher concentrations, the sweetness intensity of the synthetic sweeteners increases at a lower rate than that which occurs with sugars. This has been ascribed to the bitterness and strong aftertaste that appears at these relatively high concentrations.

Cyclamates were first synthesized in 1939 and were approved for use in foods in the United States in 1950. Continued tests on the safety of these compounds resulted in the 1967 finding that cyclamate can be converted by intestinal flora into cyclohexylamine, which is a carcinogen. Apparently, only certain individuals have the ability to convert cyclamate to cyclohexylamine (Collings 1971). In a given population, a portion are nonconverters, some convert only small amounts, and others convert large amounts.

Aspartame is a dipeptide derivative, L-aspartyl-L-phenylalanine methyl ester, which was approved in the United States in 1981 for use as a tabletop sweetener, in dry beverage mixes, and in foods that are not heat processed. This substance is metabolized in the body to phenylalanine, aspartic acid, and methanol. Only people with phenylketonuria cannot break down



Acesulfame K

Advantame

Aspartame

Saccharin

Sucralose

Neotame

Mogroside V

Stevoside

Fig. 15.8 Chemical structure of approved intense sweeteners

phenylalanine. Another compound, diketopiperazine, may also be formed. However, no harmful effects from this compound have been demonstrated. The main limiting factor in the use of aspartame is its lack of heat stability (Homler 1984).

Acesulfame K is the potassium salt of 6-methyl-1,2,3-oxathiozine-4(3H)-one-2, 2-dioxide (Fig. 15.8). It is a crystalline powder that is about 200 times sweeter than sugar. The sweetening power depends to a certain degree on the acidity of the food it is used in. Acesulfame K is reportedly more stable than other sweeteners. The sweet taste is clean and does not linger. Sucralose is a trichloroderivative of the C-4 epimer galactosucrose. It is about 600 times sweeter than sucrose and has a similar taste profile. One of its main advantages is heat stability, so it can be used in baking.

Table 15.7 Summarizes the regulatory status, brand names and applications of currently available intense sweeteners.

Stevioside and mogroside are glycosides of phenolic groups as can be seen in Fig. 15.6. Blending of nonnutritive sweeteners may lead to improved taste, longer shelf life, lower production cost, and reduced consumer exposure to any single sweetener (Verdi and Hood 1993).

Phosphates

These compounds are widely used as food additives, in the form of phosphoric acid as acidulant, and as monophosphates and polyphosphates in a large number of foods and for a variety of purposes.

Table 15.7 Regulatory stauus, brand names, relative sweetness and daily intake for currently approved intense sweeteners

Sweetener	Regulatory status	Examples of brand names containing sweetener	Sweetness intensity compared to sucrose	ADI
Acesulfame potassium (Ace-K)	Approved as a sweetener and flavor enhancer in foods generally (except in meat and poultry) 21 CFR 172.800	Sweet One® Sunett®	200×	15
Advantame	Approved as a sweetener and flavor enhancer in foods generally (except in meat and poultry) 21 CFR 172.803		20,000×	32.8
Aspartame	Approved as a sweetener and flavor enhancer in foods generally 21 CFR 172.804	Nutrasweet® Equal® Sugar Twin®	200×	50
Neotame	Approved as a sweetener and flavor enhancer in foods generally (except in meat and poultry) 21 CFR 172.829	Newtame®	7000–13,000×	0.3
Saccharin	Approved as a sweetener only in certain special dietary foods and as an additive used for certain technological purposes 21 CFR 180.37	Sweet and Low® Sweet Twin® Sweet'N Low® Necta Sweet®	200–700×	15
Mogroside Siraitia grosvenorii Swingle extracts (SGFE)	SFGE containing 25%, 45% or 55% Mogroside V is the subject of GRAS notices for specific conditions of use GRAS Notice Inventory	Nectresse® Monk Fruit in the Raw® PureLo®	100–250×	NS
Certain high purity steviol glycosides purified from the leaves of *Stevia rebaudiana*(Bertoni) Bertoni	≥95% pure glycosides Subject of GRAS notices for specific conditions of use GRAS Notice Inventory	Truvia® PureVia® Enliten®	200–400×	4
Sucralose	Approved as a sweetener in foods generally 21 CFR 172.831	Splenda®	600×	5

ADI Acceptable daily Intake in milligrams per kilogram body weight per day (mg/kg bw/d)
Adapted from: http://www.fda.gov/Food/IngredientsPackagingLabeling/FoodAdditivesIngredients/ucm397725.htm#Luo_Han_Guo_fruit_extracts

Phosphates serve as buffering agents in dairy, meat, and fish products; anticaking agents in salts; firming agents in fruits and vegetables; yeast food in bakery products and alcoholic beverages; and melting salts in cheese processing. Phosphorus oxychloride is used as a starch-modifying agent.

The largest group of phosphates and the most important in the food industry is the orthophosphates (Fig. 15.9). The phosphate group has three replaceable hydrogens, giving three possible sodium orthophosphates—monosodium, disodium, and trisodium phosphate. The phosphates can be divided into orthophosphates, polyphosphates, and metaphosphates, the latter having little

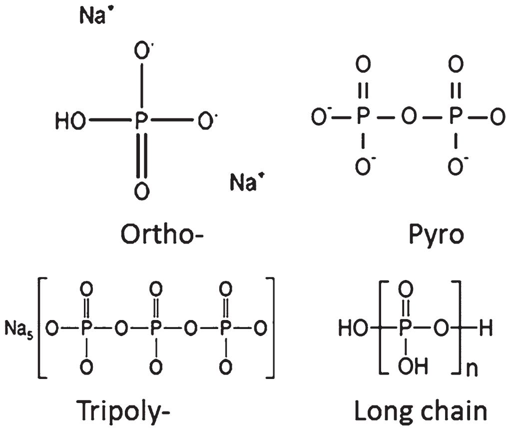


Fig. 15.9 Structure of ortho- and polyphosphate salts

practical importance. Polyphosphates have two or more phosphorus atoms joined by an oxygen bridge in a chain structure. The first members of this series are the pyrophosphates, which have one P-O-P linkage. The condensed phosphate with two linkages is tripolyphosphate. Alkali metal phosphates with chain lengths greater than three are usually mixtures of polyphosphates with varied chain lengths. The best known is sodium hexametaphosphate. The longer chain length salts are glasses. Hexametaphosphate is not a real metaphosphate, since these are ring structures and hexametaphosphate is a straight-chain polyphosphate. Sodium hexametaphosphate has an average chain length of 10–15 phosphate units.

Phosphates are important because they affect the absorption of calcium and other elements. The absorption of inorganic phosphorus depends on the amount of calcium, iron, strontium, and aluminum present in the diet. Chapman and Pugsley (1971) have suggested that a diet containing more phosphorus than calcium is as detrimental as a simple calcium deficiency. The ratio of calcium to phosphorus in bone is 2 to 1. It has been recommended that in early infancy, the ratio should be 1.5 to 1; in older infants, 1.2 to 1; and for adults, 1 to 1. The estimated annual per capita intake in the United States is 1 g Ca and 2.9 g P, thus giving a ratio of 0.35. The danger in raising phosphorus levels is that calcium may become unavailable.

Coloring Agents

In the United States two classes of color additives are recognized: colorants exempt from certification and colorants subject to certification. The former are obtained from vegetable, animal, or mineral sources or are synthetic forms of naturally occurring compounds. The latter group of synthetic dyes and pigments is covered by the Color Additives Amendment of the U.S. Food, Drug and Cosmetic Act. In the United States these color compounds are not known by their common names but as FD&C colors (Food, Drug and Cosmetic colors) with a color and a number (Noonan 1968). As an example, FD&C red dye no. 2 is known as amaranth outside the United States. Over the years the originally permitted fat-soluble dyes have been removed from the list of approved dyes, and only water-soluble colors remain on the approved list (Newsome 1990).

Color additives listed in 21 CFR Parts 74 must be analyzed and batch certified by FDA before they can be used in any food in the United States. This requirement applies to products imported into this country as well as those manufactured domestically. Straight colors required to be certified are listed in 21 CFR Part 74. Most lakes are provisionally listed under 21 CFR 81.1 for use as listed in 21 CFR 82.51 (food, drugs, and cosmetics), All FD&C Red No. 40 lakes are permanently listed under 21 CFR 74.340 (food),. FD&C Table 15.8 summarizes the approved colors which are exempt from batch certification. Colors requiring batch certification are included in Table 15.9.

Lakes are insoluble forms of the dyes and are obtained by combining the color with aluminum or calcium hydroxide. The dyes provide color in solution, and the lakes serve as insoluble pigments.

Food Irradiation

Food irradiation is the treatment of foods by ionizing radiation in the form of beta, gamma, or X-rays. The purpose of food irradiation is to preserve food and to prolong shelf life, as other processing techniques such as heating or drying have done. For regulatory purposes irradiation is considered a process, but in many countries it is considered to be an additive. This inconsistency in the interpretation of food irradiation results in great obstacles to the use of this process and has slowed down its application considerably. Several countries are now in the process of reconsidering their legislation regarding irradiation. Depending on the radiation dose, several applications can be distinguished. The unit of radiation is the Gray (Gy), which is a measure of the energy absorbed by the food. It replaced the older unit rad (1 Gy = 100 rad).

Table 15.8 Color additives approved for use in human food Part 73, Subpart A: Color additives exempt from batch certification

21 CFR section	Straight color	Year approved	Uses and restrictions
§73.30	Annatto extract	1963	Foods generally
§73.40	Dehydrated beets (beet powder)	1967	Foods generally
§73.75	Canthaxanthin(3)	1969	Foods generally, NTE(7) 30 mg/lb of solid or semisolid food or per pint of liquid food; May also be used in broiler chicken feed
§73.85	Caramel	1963	Foods generally
§73.90	β-Apo-8′-carotenal	1963	Foods generally, NTE(7): 15 mg/lb solid, 15 mg/pt liquid
§73.95	β-Carotene	1964	Foods generally
§73.100	Cochineal extract	1969	Foods generally
		2009	Food label must use common or usual name "cochineal extract"; effective January 5, 2011
	Carmine	1967	Foods generally
		2009	Food label must use common or usual name "carmine"; effective January 5, 2011
§73.125	Sodium copper chlorophyllin(3)	2002	Citrus-based dry beverage mixes NTE(7) 0.2% in dry mix; extracted from alfalfa
§73.140	Toasted partially defatted cooked cottonseed flour	1964	Foods generally
§73.160	Ferrous gluconate	1967	Ripe olives
§73.165	Ferrous lactate	1996	Ripe olives
§73.169	Grape color extract(3)	1981	Non-beverage food
§73.170	Grape skin extract (enocianina)	1966	Still & carbonated drinks & ades; beverage bases; alcoholic beverages (restrict. 27 CFR Parts 4 & 5)
§73.200	Synthetic iron oxide(3)	1994	Sausage casings NTE(7) 0.1% (by wt)
		2015	Hard and soft candy, mints and chewing gum
		2015	For allowed human food uses, reduce lead from ≤20 ppm to ≤5 ppm
§73.250	Fruit juice(3)	1966	Foods generally
		1995	Dried color additive
§73.300	Carrot oil	1967	Food generally
§73.340	Paprika	1966	Food Generally
§73.345	Paprika oleoresin	1966	Food generally
§73.350	Mica-based pearlescent pigments	2006	Cereals, confections and frostings, gelatin desserts, hard and soft candies (including lozenges), nutritional supplement tablets and gelatin capsules, and chewing gum
		2013	Distilled spirits containing not less than 18% and not more than 23% alcohol by volume but not including distilled spirits mixtures containing more than 5% wine on a proof gallon basis
		2015	Cordials, liqueurs, flavored alcoholic malt beverages, wine coolers, cocktails, nonalcoholic cocktail mixers and mixes and in egg decorating kits
§73.450	Riboflavin	1967	Foods generally
§73.500	Saffron	1966	Foods generally
§73.530	Spirulina extract	2013	Candy and chewing gum
		2014	Coloring confections (including candy and chewing gum), frostings, ice cream and frozen desserts, dessert coatings and toppings, beverage mixes and powders, yogurts, custards, puddings, cottage cheese, gelatin, breadcrumbs, and ready-to-eat cereals (excluding extruded cereals)
§73.575	Titanium dioxide	1966	Foods generally; Not to exceed 1% by wt
§73.585	Tomato lycopene extract; tomato lycopene concentrate(3)	2006	Foods generally
§73.600	Turmeric	1966	Foods generally
§73.615	Turmeric oleoresin	1966	Foods generally

http://www.fda.gov/ForIndustry/ColorAdditives/ColorAdditiveInventories/ucm115641.htm#table4A

Table 15.9 Color additives approved for use in human food Part 74, Subpart A: Color additives subject to batch certification

21 CFR section	Straight color	Year approved	Uses and restrictions
§74.101	FD&C Blue No. 1	1969	Foods generally
		1993	Added Mn spec
§74.102	FD&C Blue No. 2	1987	Foods generally
§74.203	FD&C Green No. 3	1982	Foods generally
§74.250	Orange B(3)	1966	Casings or surfaces of frankfurters and sausages; NTE(7) 150 ppm (by wt)
§74.302	Citrus Red No. 2	1963	Skins of oranges not intended or used for processing; NTE(7) 2.0 ppm (by wt)
§74.303	FD&C Red No. 3	1969	Foods generally
§74.340	FD&C Red No. 40(3)	1971	Foods generally
§74.705	FD&C Yellow No. 5	1969	Foods generally
§74.706	FD&C Yellow No. 6	1986	Foods genera

http://www.fda.gov/ForIndustry/ColorAdditives/ColorAdditiveInventories/ucm115641.htm#table4A

Radiation sterilization produces foods that are stable at room temperature and requires a dose of 20–70 kGy. At lower doses, longer shelf life may be obtained, especially with perishable foods such as fruits, fish, and shellfish. The destruction of *Salmonella* in poultry is an application for radiation treatment. This requires doses of 1–10 kGy. Radiation disinfestation of spices and cereals may replace chemical fumigants, which have come under increasing scrutiny in recent years. Dose levels of 8–30 kGy would be required. Other possible applications of irradiation processing are inhibition of sprouting in potatoes and onions and delaying of the ripening of tropical fruits.

Nutrition Supplements

There are two fundamental reasons for the addition of nutrients to foods consumed by the public: (1) to correct a recognized deficiency of one or more nutrients in the diets of a significant number of people when the deficit actually or potentially adversely affects health; and (2) to maintain the nutritional quality of the food supply at a level deemed by modern nutrition science to be appropriate to ensure good nutritional health, assuming only that a reasonable variety of foods are consumed (Augustin and Scarbrough 1990).

A variety of compounds are added to foods to improve the nutritional value of a product, to replace nutrients lost during processing, or to prevent deficiency diseases. Most of the additives in this category are vitamins or minerals. Enrichment of flour and related products is now a well-recognized practice. The U.S. Food and Drug Administration (FDA) has established definitions and standards of identity for the enrichment of wheat flour, farina, com meal, com grits, macaroni, pasta products, and rice. These standards define minimum and maximum levels of addition of thiamin, riboflavin, niacin, and iron. In some cases, optional addition of calcium and vitamin D is allowed. Margarine contains added vitamins A and D, and vitamin D is added to fluid and evaporated milk. The addition of the fat-soluble vitamins is strictly controlled, because of the possible toxicity of overdoses of these vitamins. The vitamin D enrichment of foods has been an important measure in the elimination of rickets. Another example of the beneficial effect of enrichment programs is the addition of iodine to table salt. This measure has virtually eliminated goiter.

One of the main potential deficiencies in the diet is calcium. Lack of calcium is associated with osteoporosis and possibly several other diseases. The recommended daily allowance for adolescents/young adults and the elderly has increased from the previous recommendation of 800–1200 mg/day to 1500 mg/day. This level is difficult to achieve, and the use of calcium citrate in fortified foods has been recommended by Labin-Goldscher and Edelstein (1996). Sloan and Stiedemann (1996) highlighted the relationship between consumer demand for fortified products and complex regulatory issues.

Migration from Packaging Materials

When food packaging materials were mostly glass or metal cans, the transfer of packaging components to the food consisted predominantly of metal (iron, tin, and lead) uptake. With the advent of extensive use of plastics, new problems of transfer of toxicants and flavor and odor substances became apparent. In addition to polymers, plastics may contain a variety of other chemicals, catalysts, antioxidants, plasticizers, colorants, and light absorbers. Depending on the nature of the food, especially its fat content, any or all of these compounds may be extracted to some degree into the food (Bieber et al. 1985).

Awareness of the problem developed in the mid-1970s when it was found that mineral waters sold in polyvinyl chloride (PVC) bottles contained measurable amounts of vinyl chloride monomer. Vinyl chloride is a known carcinogen. The Codex Alimentarius Committee on Food Additives and Contaminants has set a guideline of 1 ppm for vinyl chloride monomer in PVC packaging and 0.01 ppm of the monomer in food (Institute of Food Technologists 1988). Another additive found in some PVC plastics is octyl tin mercaptoacetate or octyl tin maleate. Specific regulations for these chemicals exist in the Canadian Food and Drugs Act.

The use of plastic netting to hold and shape meat during curing resulted in the finding of N-nitrosodiethylamine and N-nitrosodibutylamine in hams up to levels of 19 ppb (parts per billion) (Sen et al. 1987). Later research established that the levels of nitrosamines present were not close to violative levels (Marsden and Pesselman 1993).

Plasticizers, antioxidants, and colorants are all potential contaminants of foods that are contained in plastics made with these chemicals. Control of potential migration of plastic components requires testing the containers with food simulants selected to yield information relevant to the intended type of food to be packaged (DeKruyf et al. 1983; Bieber et al. 1984).

Incidental Additives or Contaminants

Pesticides

Contamination of food with residues of pesticides may result from the application of these chemicals in agricultural, industrial, or household use. Nearly 300 organic pesticides are in use, including insecticides, miticides, nematocides, rodenticides, fungicides, and herbicides. The most likely compounds to appear as food contaminants are insecticides, of which there are two main classes—chlorinated hydrocarbon insecticides and organophosphorous insecticides.

The chlorinated hydrocarbon insecticides can be divided into three classes—oxygenated compounds, benzenoid nonoxygenated compounds, and nonoxygenated nonben-zenoid compounds (Table 15.10) (Mitchell 1966). In addition to the pesticide compounds, there may be residues of their metabolites, which may be equally toxic. Two important properties of the chlorinated hydrocarbons are their stability, which leads to persistence in the environment, and their solubility in fat, which results in their deposition and accumulation in fatty tissues. The structure of some of the chlorinated hydrocarbon insecticides is given in Fig. 15.10. Aldrin is a technical com-

Table 15.10 Classes of chlorinated hydrocarbon insecticides

Class I—Oxygenated compounds	
Chlorobenzilate	Methoxychlor
Dicofol	Neotran
Dieldrin	Ovex
Endosulfan	Sulfenone
Endrin	Tetradifon
Kepone	
Class II—Benzenoid, nonoxygenated compounds	
BHC	Perthane
Chlorobenside	TDE
DDT	Zectran
Lindane	
Class III—Nonoxygenated, nonbenzenoid compounds	
Aldrin	Mirex
Chlordan	Strobane
Heptachlor	Toxaphene

Source: From L.E. Mitchell, Pesticides: Properties and Prognosis, in *Organic Pesticides in the Environment*, R.F. Gould, ed., 1966, American Chemical Society

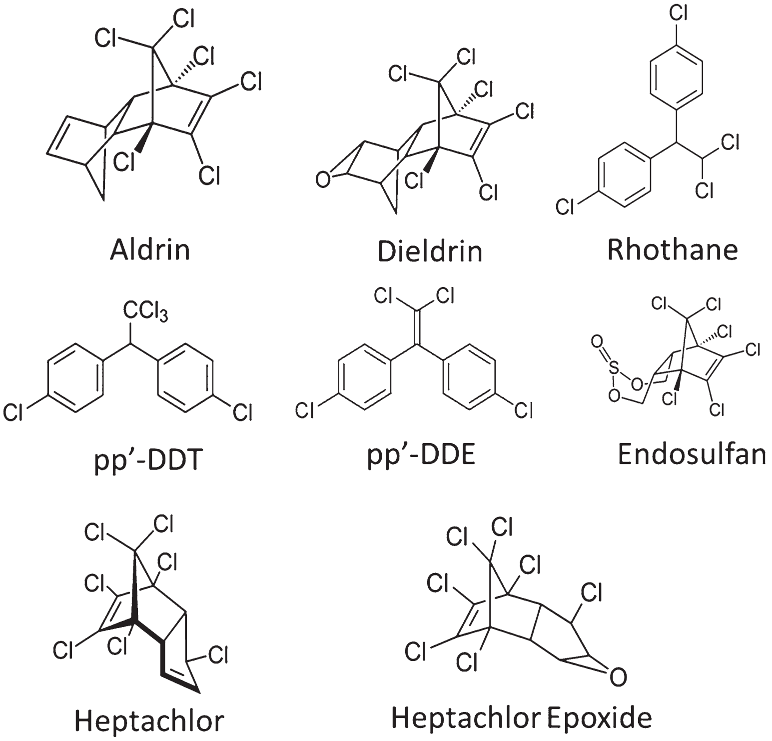


Fig. 15.10 Structure of some chlorinated hydrocarbon pesticides

pound containing about 95% of the compound 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-exo-1,4-*endo*-exo-5,8-dimethanonaphthalene. It has a molecular weight of 365, formula $C_{12}H_8Cl_6$, and contains 58% chlorine. Residues of this compound in animal and plant tissues are converted into dieldrin by epoxidation. The epoxide is the stable form and, thus, it is usual to consider these compounds together.

Dieldrin contains about 85% of the compound 1, 2, 3, 4, 10, 10-hexachloro-6, 7-epoxy-1, 4, 4a, 5, 6, 7, 8, 8a-octahydro-exo-l, 4-endo-exo-5, 8-dimethano-naphthalene (HEOD). It has a molecular weight of 381, formula $C_{12}H_8Cl_6O$, and contains 56% chlorine. DDT is a technical compound that contains about 70% of the active ingredient pp′-DDT. In addition, there are other isomers, including op′-DDT, as well as related compounds such as TDE or rhothane. The insecticide pp′-DDT is 1,1,1-trichloro-2,2-di-(4-chlorophenyl) ethane, formula $C_{14}H_9Cl_5$. It has a molecular weight of 334.5 and contains 50% chlorine. Residues of DDT in animal tissue are slowly dehydrochlorinated to pp’-DDE, which may occur at levels of up to 70% of the original DDT. It is usual to combine DDT, DDE, and TDE in one figure as “total DDT equivalent.”

Heptachlor contains about 75% of 1,4,5,6,7,10,10-heptachloro-4,7,8,9-tetrahyro-4,7-methyleneindene, formula $C_{10}H_5Cl_7$. It has a molecular weight of 373.5 and contains 67% chlorine. In animal and plant tissues, it epoxidizes to heptachlor epoxide, which is analogous in structure to HEOD (dieldrin).

The organophosphorous insecticides are inhibitors of Cholinesterase and, because of their water solubility and volatility, create less of a problem as food contaminants than the chlorinated hydrocarbons. A large number of organophosphorous insecticides are in use; these can act by themselves or after oxidative conversions in plants and animals (Table 15.11). The water solubility of these compounds varies widely, as is indicated by Table 15.12. The organophosphorous insecticides may be subject to oxidation, hydrolysis, and demethylation (Fig. 15.11). Thiophosphates may be changed to sulfoxides and sulfones in animals and plants.

Table 15.11 Classification of organophosphorous insecticides

Aliphatic derivatives	
Butonate	Mevinphos
Demeton	Mipefox
Dichlorvos	Naled
Dimefox	Phorate
Dimethoate	Phosphamidon
Dithiodemeton	Schradan
Ethion	Sulfotepp
Malathion	Tepp
Methyl demeton	Trichlorofon
Aromatic (Cyclic) derivatives	
Azinphosmethyl	EPN
Carbophenothion	Fenthion
Diazinon	Methyl parathion
Dicapthon	Parathion
Endothion	Ronnel

Source: From L.E. Mitchell, Pesticides: Properties and Prognosis, in *Organic Pesticides in the Environment*, R.F. Gould, ed., 1966, American Chemical Society

Table 15.12 Water solubilities of some organophosphorus insecticides

Insecticide	(ppm)
Carbophenothion	2
Parathion	24
Azinphosmethyl	33
Diazinon	40
Methyl parathion	50
Phorate	85
Malathion	145
Dichlorvos	1000
Dimethoate	7000
Mevinphos	∞

Source: From L.E. Mitchell, Pesticides: Properties and Prognosis, in *Organic Pesticides in the Environment,* R.F. Gould, ed., 1966, American Chemical Society

In animal products, chlorinated hydrocarbon residues are predominantly present in the lipid portion, organophosphates in both lipid and aqueous parts. In plant materials, the residue of chlorinated hydrocarbons are mostly surface bound or absorbed by waxy materials, but some can be translocated to inner parts. Extensive research has demonstrated that processing methods such as washing, blanching, heating, and canning may remove large proportions of pesticide residues (Liska and Stadelman 1969; Farrow et al. 1969). A summary of how different food processing approaches can influence pesticide residue in foods are found in Table 15.13. It is important to recognize that levels of pesticides can be lowered during processing but complete removal is unlikely.

It has been reported (Farrow et al. 1969) that 48% of DDT residues on spinach and 91% on tomatoes are removed by washing. Elkins (1989) reported that washing and blanching reduced carbaryl residues on spinach and broccoli by 97% and 98%, respectively. Washing, blanching, and canning reduced carbaryl pesticides on tomatoes and spinach by 99%. Although this pattern of removal generally holds true, Peterson et al. (1996) have pointed out that there are exceptions. Pesticides may accumulate in one part of an agricultural product. Friar and Reynolds (1991) reported that baking does not result in a decline in thiabendazole residues in potatoes, and Elkins et al. (1972) found that thermal processing does not result in a reduction of methoxychlor residues on apricots. Sometimes processing may cause a chemical to degrade, producing a compound that is more toxic than the original one.

The dietary intake of pesticide chemicals from foods is well below the acceptable daily intake (ADI) levels set by the FAO/WHO (Table 15.14). In recent years, severe restrictions on the use of many chlorinated hydrocarbon pesticides have been instituted in many areas. It can be seen that in most cases the allowable daily intake is at least one order of magnitude than the No Observed Effect Level, constituting a reasonable degree of safety.

Dioxin

The term dioxin is used to represent two related groups of chlorinated organic compounds, polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) (Fig. 15.12). A total of eight carbon atoms in each molecule can carry chlorine substitution, which produces 75 possible isomers for PCDD and 135 for PCDF.

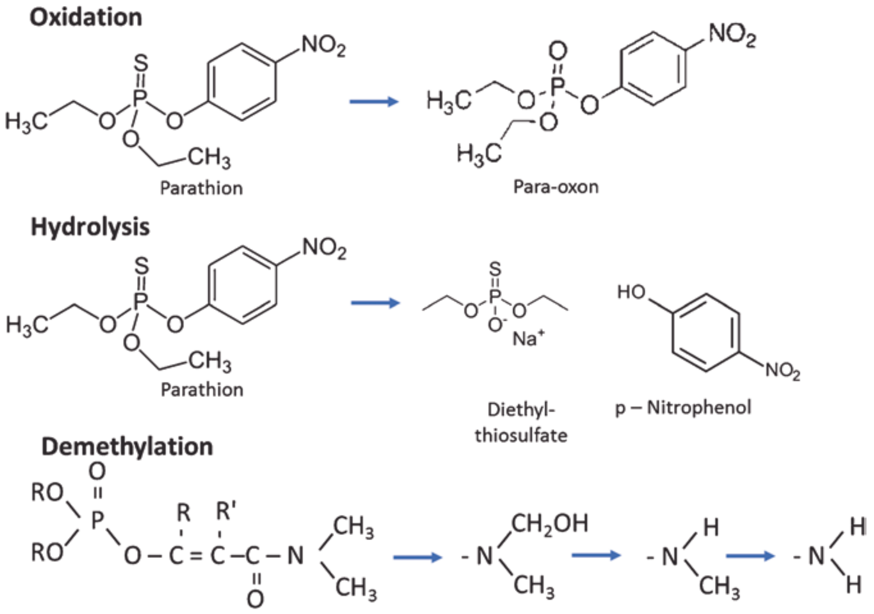


Fig. 15.11 Oxidation, hydrolysis, and demethylation reactions of organophosphorous insecticides. *Adapted from* L.E. Mitchell, Pesticides: Properties and Prognosis, in *Organic Pesticides in the Environment*, R.F. Gould, ed., 1966, American Chemical Society

These compounds are lipophilic, have low volatility, and are extremely stable. They are also very toxic, although the toxicity of each isomer may vary widely. These compounds may exhibit acute toxicity, carcinogenicity, and teratogenicity (birth defects). They are ubiquitous environmental contaminants and are present in human tissues.

The dioxins are produced as contaminants in the synthesis of certain herbicides and other chlorinated compounds, as a result of combustion and incineration, in the chlorine bleaching of wood pulp for paper making, and in some metallurgical processes (Startin 1991). Dioxins first attracted attention as a contaminant of the herbicide 2,4,5-trichloro-phenoxyacetic acid (2,4,5-T). The particular compound identified was 2,3,7,8-TCDD, which was for some time associated with the name *dioxin.* This compound was present in substantial concentration in the defoliant “Agent Orange” used by U.S. forces during the war in Vietnam.

The various isomers, also known as congeners, vary in toxicity with the 2,3,7,8-substituted ones being the most toxic. Humans appear to be less sensitive than other species.

Dioxins can be generated from chlorine bleaching of wood pulp in the paper- and cardboard-making process. This can not only lead to environmental contamination but also to incorporation of the dioxins in the paper used for making coffee filters, tea bags, milk cartons, and so forth. Dioxins can migrate into milk from cartons, even if the cartons have a polyethylene plastic coating. Unbleached coffee filters and cardboard containers have been produced to overcome this problem, and there have also been improvements in the production of wood pulp using alternative bleaching agents. The FDA guideline for dioxin in fish is 25 parts per trillion (Cordle 1981). Dioxin is considered a very potent toxin, but information on harmful effects on humans is controversial.

Polychlorinated Biphenyls (PCBs)

The PCBs are environmental contaminants that are widely distributed and have been found as residues in foods. PCBs are prepared by chlorination of biphenyl, which results in a mixture of

Table 15.13 Influence of various types of food processing on reduction of residual pesticide levels in foods (adapted from Kaushik et al. 2009)

Commodity	Pesticide	Process	Initial ppm	Final ppm	% Loss by Dissipation	Reason	References
Potato	Profenofos	Baking microwave oven	11.48	0.22		Loss of pesticide due to physico-chemical processes, e.g., evaporation, codistillation, and thermal degradation	Sharma et al. (2005)
				0.19			
Wheat flour	Endosulfan	Bread making			70	Bread makingprocess involves yeast-mediated fermentation and baking which contribute to degradation of pesticides	Sharma et al. (2005)
	Deltamethrin				63		
	Malathion				60		
	Propiaconazole				52		
	Chlorpyriphos				51		
	Hexaconazole				46		
Milk	Leptophos	Cheese making	100	1.84		Heating and salting stages in cheese making caused the greatest degradation of leptophos	Abu-Elamayem et al. (1979)
	Leptophos-oxon			0.76			
	Phenol derivative			32.26			
Rice	Ekalux 25 EC	Parboiling	0.078		49	Inactivation or degradation of the pesticides during parboiling at high temperature	Krishnamurthy and Sreeramulu (1982)
	Dursbsan 25 EC		3 to 0.042		51		
	Lebaycid ECO all (0.05%)		6		68		
Rough rice	Malathion	Parboiling	14	0.013			Cogburn et al. (1990)
Maize and beans	Malathion	12 Months storage open basket	7.73		64	Volatilization and possible settling of pesticide dust formulation to the bottom and on the sides of basket during storage in the open and windy tropical laboratory	Lalah and Wandiga (2002)
			7.52		47		
Tomatoes	HCB	Wash with acetic acid			42.9	Reduction by dissolution of phosalone in water	Mergnat et al. (1995) residue
	Lindane				46.1	Effectiveness of washing in removing residues depends upon:	Holland et al. (1994)
	p,p-DDT				27.2	1. Location of residue	
	Dimethoate				90.8	2. Age of the residue	
	Profenofos				82.4	3. Water solubility of the pesticide	
	Pirimiphos-Methyl				91.4	4. Temperature and type of wash	
						5. Effectiveness of washing may be improved addition of a detergent	
Tomatoes	HCB	Wash with tap water			9.62		
	Lindane				15.3		
	p,p-DDT				9.17		
	Dimethoate				18.8		
	Profenofos				22.7		
	Pirimiphos-Methyl				16.2		

Table 15.14 The use, allowable daily intake and NOAEL levels for some pesticides and herbicides

Compound	Use	ADI (mg/kg bw)	NOAEL
Aldrin	Insecticide	0.0001	0.025
Carbamyl	Insecticide	0.01	0.06
Chlordane	Insecticide	0.0005	0.05
Cycloxydim	Herbicide	0.07	7
DDT	Insecticide	0.02	0.25
Diazinon	Herbicide	0.002	0.025
Dieldrin	Insecticide	0.0001	0.025
Diquat	0.002	0.19	
Glyphosate	Herbicide	0.3	31
Heptachlor-heptachlor epoxide	Insecticide	0.0001	0.025
Lindane	Insecticide	0.008	0.75
Malathion	Insecticide	0.02	0.2
Methoxychlor	Insecticide	0.1	10
Paraquat	Insecticide	0.004	1.6
Parathion	Insecticide	0.005	0.05
Pyrethrins	Insecticide	0.04	10
2,4,D	Herbicide	0.3	31
2,4,5-T	Herbicide	0.03	3

Adapted from Lu 1995

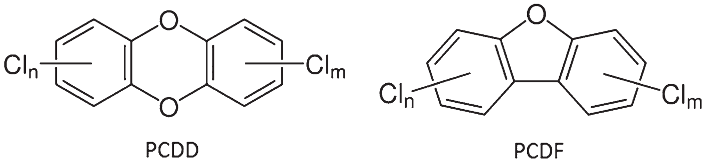


Fig. 15.12 Chemical structure of Polychlorinated Dibenzo-*p*-dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF)

isomers that have different chlorine contents. In North America, the industrial compounds are known as Aroclor; these are used industrially as dielectric fluids in transformers, as plasticizers, as heat transfer and hydraulic fluids, and so forth. The widespread industrial use of these compounds results in contamination of the environment through leakages and spills and seepage from garbage dumps. The PCBs may show up on chromatograms at the same time as chlorinated hydrocarbon pesticides. The numbering system used in PCBs and the prevalent substitution pattern are presented in Fig. 15.13. Table 15.15 presents information on commercial Aroclor compounds. In the years prior to 1977 production of PCBs in North America amounted to about 50 million pounds per year. PCBs were first discovered in fish and wildlife in Sweden in 1966, and they can now be found in higher concentrations in fish than organochlorine pesticides (Zitco 1971).

PCBs decompose very slowly. It is estimated that between 1929 and 1977, about 550 million kg of PCBs were produced in the United States. Production was stopped voluntarily after a serious poisoning occurred in Japan in 1968. Large amounts are still present in, for example, transformers and could enter the environment for many years. Federal regulations specify the following limits in foods: 1.5 ppm in milk fat, 1.5 ppm in fat portion of manufactured dairy products, 3 ppm in poultry, and 0.3 ppm in eggs. The tolerance level for PCB in fish was reduced from 5 to 2 ppm in 1984. Although there has been a good deal of concern about the possible toxicity

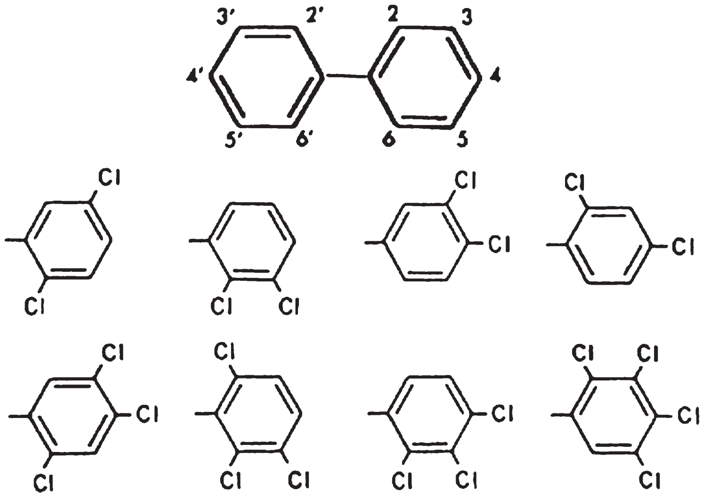


Fig. 15.13 The numbering system used in PCBs and the prevalent substitution patterns of chlorine

Table 15.15 Information on aroclor preparations

Aroclor	% Cl	Average number of Cl per molecule	Average molecular weight
Aroclor 1221	21	1.15	192
Aroclor 1232	32	2.04	221
Aroclor 1242	42	3.10	261
Aroclor 1248	48	3.90	288
Aroclor 1254	54	4.96	327
Aroclor 1260	60	6.30	372
Aroclor 1262	62	6.80	389
Aroclor 1268	68	8.70	453

of PCBs, there is now evidence that PCBs are much less toxic than initially assumed (American Council on Science and Health 1985).

Zabik and Zabik (1996) have reviewed the effect of processing on the removal of PCBs from several foods. In the processing of vegetable oil the PCB present in the crude oil was completely removed; some was removed by the hydrogenation catalyst, but most was lost by deodorization. The PCB was recovered in the deodorizer distillate.

Antibiotics

Growth-retarding or antimicrobial substances may be present in foods naturally, may be produced in a food during processing, or may occur incidentally through the treatment of diseased animals. The latter problem has created the greatest concern. The use of antibiotics in therapy, prophylaxis, and growth promotion of animals may result in residues in foods. These residue levels rarely exceed the range of 1–0.1 ppm (where toxicological interest ceases). However, levels well below those of toxicological interest may be important in food processing, for example, in cheese making, by preventing starter development. The low levels may also be important in causing allergies and development of resistant organisms. Highly sensitized persons may experience allergic reactions from milk that contains extremely low amounts of penicillin. The various antibiotics used in agriculture, including some used in food processing, are listed in Table 15.16 The tetracyclines, CTC and OTC, are broad-spectrum antibiotics and act against both gram-positive and gram-negative bacteria. The action is bacteriostatic and not bactericidal. The tetracyclines have been used to delay spoilage in poultry and fish. Their effectiveness seems to decrease quite rapidly, because the contaminating flora quickly become resistant. Nisin, which is one of the few antibiotics not used in human therapeutics, has been found to be effective as an aid in heat sterilization of foods. It is a polypeptide with a molecular weight of about 7000 and contains 18 amino acid residues. It is active against certain gram-positive organisms only, and all spores are sensitive to it.

Table 15.16 Antibiotics used in animal production

Drug	Desired effect in animals	References
Bambermycin	Improves feed conversion ratio and weight gain in chickens, beef cattle, swine, and turkeys	Reinhardt (2012) and Allen and Stanton (2014)
Lasalocid	Improves feed conversion ratio and weight gain in beef cattle	Reinhardt (2012) and Allen and Stanton (2014)
Monensin	Increase feed conversion and weight gain in beef cattle and sheep	Reinhardt (2012)
	Improves milk production in dairy cows	Allen and Stanton (2014)
Salinomycin	Increase weight gain in chickens	Reinhardt (2012)
Virginiamycin	Improved feed conversion and weight gain in chickens, swine, turkeys, and beef cattle	Reinhardt (2012) and Allen and Stanton (2014)
Bacitracin	Increase weight gain in chickens, turkeys, beef cattle, and swine; promotes egg production in chickens	Reinhardt (2012) and Allen and Stanton (2014)
Carbadox	Increases feed conversion and weight gain in swine	Allen and Stanton (2014)
Laidlomycin	Increase feed conversion and weight gain in beef cattle	Allen and Stanton 2014
Lincomycin	Increase feed conversion ratio and weight gain in chickens and swine	Allen and Stanton (2014)
Neomycin/ oxytetracyclinee	Increase weight gain and feed conversion ratio in chickens, turkeys, swine, and beef cattle	Allen and Stanton (2014)
Penicillin	Increase feed conversion ratio and weight gain in chickens, turkeys, and swine	Allen and Stanton (2014)
Roxarsone	Increase feed conversion ratio and weight gain in chickens and turkeys	Allen and Stanton (2014)
Tylosin	Increase feed conversion ratio and weight gain in chickens and swine	Allen and Stanton (2014)

Trace Metals

A variety of trace metals (such as mercury and lead) may become components of foods through industrial contamination of the environment. Some trace metals (such as tin and lead) may be introduced into foods through pickup from equipment and containers (especially tin cans).

Mercury

Large amounts of mercury are released into the environment by several industries. Major mercury users are the chloralkali industry, where mercury is used in electrolytic cells; traditional gold extraction and the pulp and paper industry.

Mercury (Hg) occurs naturally in the Earth's crust and is present in the environment and atmosphere at low levels. Concerns about Mercury are related to its release through anthropogenic emissions. Mercury is detrimental to humans, animals and plants (Eisler 2004).

Natural sources of mercury in the environment include elemental mercury vapor from volcanoes and forest fires and the release of inorganic mercury from movement of water (Bose-O'Reilly et al. 2010). Environmental sources of Mercury include burning of coal and fossil fuels, mining of mercury, precious metal refinement, electrical and automotive part manufacture, and chemical processing, and release through waste incineration, landfills, and industrial contamination of water systems. Methylmercury (MeHg) contamination of fish is still a significant source of human exposure to mercury compounds in fish-eating populations. As much as 90% of ingested MeHg is absorbed through the intestine and forms thiol (-SH) complexes with proteins and amino acids in the liver. Some MeHg enters the general circulation, and is distributed throughout all tissues including the brain. However, most of the absorbed MeHg is incorporated into bile, secreted into the intestine, and reabsorbed through the enterohepatic circulation (Martinez-Finley and Aschner 2014).

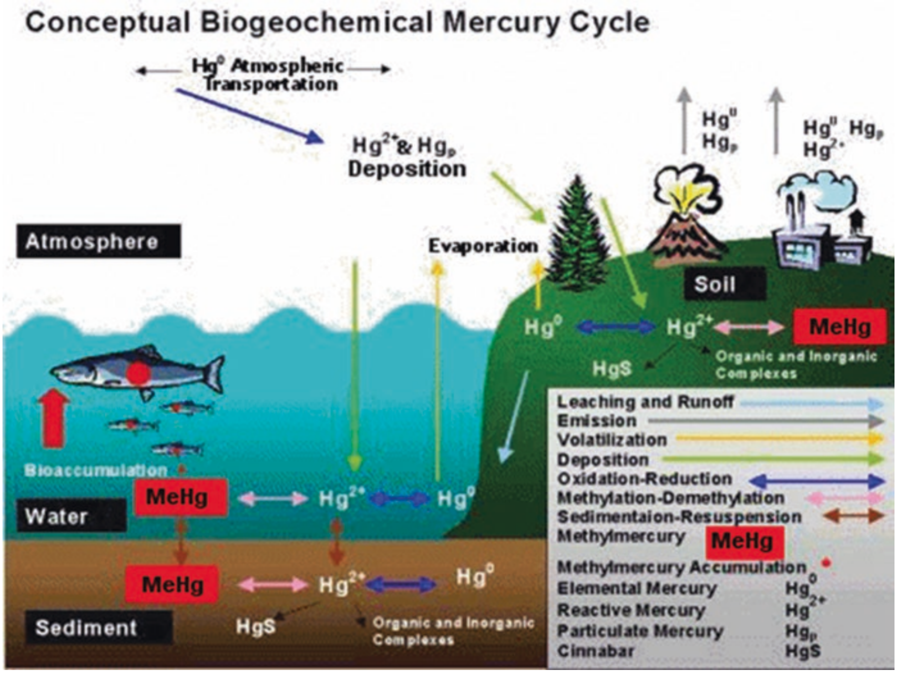


Fig. 15.14 The environmental conversion of inorganic mercury and some mercury-containing compounds to methyl mercury. *Source:* https://www.ec.gc.ca/mercure-mercury/default.asp?lang=En&n=67E16201-1#mercurymethylation

The discoveries of biomethylation and bioaccumulation aroused intense interest in the environmental fate of mercury and its pathways to human exposure. Methyl mercury is found in most fish species and in fish consuming animals including humans. The cyscle of mercury in the environment ae illustrated in Fig. 15.14 where elemental mercury is biomethylated by microorganisms in sediments found in both fresh and ocean water. Historically environmental mercury came from Chloralkali plants which discharged large amounts of inorganic mercury into rivers, lakes, and ocean bays. Other sources included paper pulp factories. These practices have been eliminated, however gold mining operations can result in large quantities of liquid mercury being deposited in river beds (Pfeiffer and Lacerda 1988).

Formation of the more volatile dimethyl mercury is favored at alkaline pH. The less volatile monomethyl form is favored at acid pH. Because much of the mercury pollution ends up in rivers and lakes where it is converted into methyl mercury, contamination of fish with mercury has been a great concern. In many animal tissues, methyl mercury may comprise as much as 99% of the total mercury present. The present interest in mercury and its effect on humans and wildlife originated with the discovery of mercury as the causative agent in the Minamata disease in Japan. Near the town of Minamata, a chemical industry used mercury compounds as catalysts for the conversion of acetylene into acetaldehyde and vinyl chloride. Organic mercury compounds were released into the waters of Minamata Bay and contaminated fish and shellfish. Many cases of mercury poisoning occurred, resulting in the death of close to 50 patients. This event triggered research into mercury contamination in many areas of the world. As a result, there is now much improved control of environmental release of mercury. It should be noted that some natural sources such as volcanic eruptions still contribute to volatile mercury being released to the environment.

Fresh and saltwater seafood remain the largest dietary source of mercury. The higher the species in the food chain the greater the bioaccumulation. The US. FDA has summarized th mercury levels in commercial fish and shell fish over the period of 1990–2012. Table 15.17 summarizes the FDA report.

Table 15.17 Mercury concentration found in fish. http://www.fda.gov/Food/FoodborneIllnessContaminants/Metals/ucm115644.htm

Species	Mean (PPM)	Minimum (PPM)	Maximum (PPM)	Num. of samples	Data source
Anchovies	0.016	ND	0.049	15	FDA 2007–2009
Bass (Saltwater, Black, striped, rockfish)	0.167	ND	0.96	101	FDA 1991–2010
Bass chilean	0.354	ND	2.18	74	FDA 1994–2010
Bluefish	0.368	0.089	1.452	94	FDA 1991–2009
Buffalofish	0.137	0.032	0.43	17	FDA 1992–2008
Butterfish	0.058	ND	0.36	89	NMFS report 1978
Carp	0.110	ND	0.271	14	FDA 1992–2007
Catfish	0.024	ND	0.314	59	FDA 1991–2010
Clam	0.009	ND	0.028	15	FDA 1991–2010
Cod	0.111	ND	0.989	115	FDA 1991–2010
Crab	0.065	ND	0.61	93	FDA 1991–2009
Crawfish	0.033	ND	0.051	46	FDA 1991–2007
Croaker atlantic (Atlantic)	0.069	ND	0.193	90	FDA 2002–2011
Croaker white (Pacific)	0.287	0.18	0.41	15	FDA 1997
Flatfish	0.056	ND	0.218	71	FDA 1991–2009
Grouper (all species)	0.448	0.006	1.205	53	FDA 1991–2005
Haddock (Atlantic)	0.055	ND	0.197	50	FDA 1991–2009
Hake	0.079	ND	0.378	49	FDA 1994–2009
Halibut	0.241	ND	1.52	101	FDA 1992–2009
HERRING	0.078	ND	0.56	27	FDA 2005–2012
Jacksmelt	0.081	0.011	0.5	23	FDA 1997–2007
Lobster (Northern/American)	0.107	ND	0.23	9	FDA 2005–2007
Lobster (Species unknown)	0.166	ND	0.451	71	FDA 1991–2008
Lobster (Spiny)	0.093	ND	0.27	13	FDA 1991–2005
Mackerel atlantic (N.Atlantic)	0.05	0.02	0.16	80	NMFS report 1978
Mackerel chub (Pacific)	0.088	0.03	0.19	30	NMFS report 1978
Mackerel king	0.73	0.23	1.67	213	Gulf of Mexico report 2000
Mackerel spanish (Gulf of Mexico)	0.454	0.07	1.56	66	NMFS report 1978
Mackerel spanish (S. Atlantic)	0.182	0.05	0.73	43	NMFS report 1978
Mahi mahi	0.178	ND	0.45	29	FDA 1991–2005
Marlin	0.485	0.1	0.92	16	FDA 1992–1996
Monkfish	0.161	ND	0.289	11	FDA 1994–2007
Mullet	0.050	ND	0.27	20	FDA 1991–2008
Orange roughy	0.571	0.265	1.12	81	FDA 1991–2009
Oyster	0.012	ND	0.25	61	FDA 1991–2009
Perch (Freshwater)	0.150	ND	0.325	19	FDA 1991–2007
Perch ocean	0.121	ND	0.578	31	FDA 1991–2010
Pickerel	0.095	ND	0.31	16	FDA 1991–2007
Pollock	0.031	ND	0.78	95	FDA 1991–2008
Sablefish	0.361	0.09	1.052	26	FDA 2004–2009
Salmon (Canned)	0.014	ND	0.086	19	FDA 1993–2009
Salmon (Fresh/frozen)	0.022	ND	0.19	94	FDA 1991–2009
Sardine	0.013	ND	0.083	90	FDA 2002–2010
Scallop	0.003	ND	0.033	39	FDA 1991–2009

(continued)

Table 15.17 (continued)

Species	Mean (PPM)	Minimum (PPM)	Maximum (PPM)	Num. of samples	Data source
Scorpionfish	0.233	0.098	0.456	6	FDA 2006–2007
Shad	0.038	ND	0.186	15	FDA 2007–2011
Shark	0.979	ND	4.54	356	FDA 1991–2007
Sheepshead	0.090	ND	0.17	8	FDA 1992–2007
Shrimp	0.009	ND	0.05	40	FDA 1991–2009
Skate	0.137	0.04	0.36	56	NMFS REPORT 1978
Snapper	0.166	ND	1.366	67	FDA 1991–2007
Squid	0.024	ND	0.07	36	FDA 2005–2009
Swordfish	0.995	ND	3.22	636	FDA 1990–2010
Tilapia	0.013	ND	0.084	32	FDA 1991–2008
Tilefish (Atlantic)	0.144	0.042	0.533	32	FDA 1994–2004
Tilefish (Gulf of Mexico)	1.123	0.65	3.73	60	NMFS report 1978
Trout (Freshwater)	0.071	ND	0.678	35	FDA 1991–2008
Tuna (Canned, albacore)	0.350	ND	0.853	451	FDA 1991–2009
Tuna (Canned, light)	0.126	ND	0.889	545	FDA 1991–2010
Tuna (Fresh/frozen, albacore)	0.358	ND	0.82	43	FDA 1992–2008
Tuna (Fresh/frozen, All)	0.386	ND	1.816	420	FDA 1991–2010
Tuna (Fresh/frozen, bigeye)	0.689	0.128	1.816	21	FDA 1993–2005
Tuna (Fresh/frozen, skipjack)	0.144	0.022	0.26	3	FDA 1993–2007
Tuna (Fresh/frozen, species unknown)	0.410	ND	1.3	122	FDA 1991–2010
Tuna (Fresh/frozen, yellowfin)	0.354	ND	1.478	231	FDA 1993–2010
Weakfish (Sea trout)	0.235	ND	0.744	46	FDA 1991–2005
Whitefish	0.089	ND	0.317	37	FDA 1991–2008
Whiting	0.051	ND	0.096	13	FDA 1991–2008

Source of data: FDA 1990–2012, “National Marine Fisheries Service Survey of Trace Elements in the Fishery Resource” Report 1978, “The Occurrence of Mercury in the Fishery Resources of the Gulf of Mexico” Report 2000
ND-mercury concentration below detection level (Level of Detection (LOD) = 0.01 ppm)
N/A-data not available

Lead and Tin

The presence of lead in foods may be the result of environmental contamination, pickup of the metal from equipment, or the solder of tin cans. It has been estimated that nearly 90% of the ingested lead is derived from food (Somers and Smith 1971). However, only 5% of this is absorbed. In the early 1970s, the average North American car was reported to emit 2.5 kg of lead per year (Somers and Smith 1971), and Zuber et al. (1970) reported that crops grown near busy highways had a high lead content (in some cases, exceeding 100 ppm of lead in the dry matter). The removal of lead from gasoline has eliminated this source of contamination. Lead can also be picked up by acid foods such as fruit juices that are kept in glazed pottery made with lead-containing glazes. Both lead and tin may be taken up by foods from the tin of cans and from the solder used in their manufacture. The amounts of lead and tin taken up depend on the type of tin plate and solder used and on the composition and properties of the canned foods. In a study on the detinning of cans by spinach, Lambeth et al. (1969) found that detinning was significantly related to the oxalic acid content and pH of the product. Detinning in excess of 60% was observed during 9 months’ storage of high-oxalate spinach.

The present levels of lead that humans ingest cause concern because ADI calculations range from 0.1 to 0.8 mg lead per day. The average daily intake is in the vicinity of 0.4 mg lead per day. This means that lead is one of the few toxic food components for which the acceptable daily intake is approached or exceeded by the general population (Clarkson 1971).

Cadmium

As are lead and mercury, cadmium is a nonessential trace metal with high toxicity. Crustaceans have the ability to accumulate cadmium as well as other trace metals, such as zinc. Cadmium levels in oysters may reach 3–4 ppm, whereas in other foods, levels are only one-tenth or one-hundredth of these (Underwood 1973).

Arsenic

Arsenic is found in the environment from both natural and human sources. Environmental Aarsenic can come from erosion of arsenic-containing rocks, volcanic eruptions, contamination from mining and smelting ores. Environmental arsenic can contaminate food products from absorption through soil and water. Foods that are produced following prolonged contact with water, such as seafood and rice frequently have higher levels of arsenic contamination.

Arsenic is used as a pesticide primarily to preserve wood from rot and decay. Historically, arsenic was also used in rat poisons, ant poisons and weed killers. Agricultural soils can contain high levels of arsenic resulting from its former agricultural uses. Most forms of arsenic tend to stick to soil or sediment particles however, some arsenic can dissolve in water, leaching into lakes, rivers, or ground water.

Exposure to arsenic can come from many different foods and beverages. Consumer awareness of dietary arsenic exposure in a publication by Consumer Reports magazine analyzing arsenic content of commercially available fruit juices (January, 2012) and rice-based products (November, 2012). In July 2013, the FDA proposed an action level of 10 parts per billion (ppb), which is similar to the U.S. Environmental Protection agency (EPA) drinking water standard, for inorganic arsenic in apple juice. The FDA has not yet set an arsenic standard for rice-based products, however, the Joint FAO-WHO Codex Alimentarius Commission in July 2014 established a maximum level of 200 ppb for inorganic arsenic in polished rice. Based on its testing, the FDA on April 1, 2016 proposed an action level, or limit, of 100 parts per billion (ppb) for inorganic arsenic in infant rice cereal. This level, which is based on the FDA's assessment of a large body of scientific information, seeks to reduce infant exposure to inorganic arsenic.

http://www.consumerreports.org/cro/magazine/2012/11/arsenic-in-your-food/index.htm

https://medicalxpress.com/news/2015-01-arsenic-food.html#jCp

https://medicalxpress.com/news/2015-01-arsenic-food.html#jCp

Polycyclic Aromatic Hydrocarbons (PAHs)

These compounds form a large group of materials that are now known to occur in the environment. The structural formulas of the major members of this group are presented in Fig. 15.15. Several of these, especially benzo(a)pyrene (3,4-benzopyrene), have been found to be carcinogenic. Usually, the polycyclic hydrocarbons occur together in foods, especially in smoked foods, because the aromatic hydrocarbons are constituents of wood smoke. Trace quantities of PAHs have been found in a variety of foods, and this may be the result of environmental contamination.

The PAHs may be carcinogenic and mutagenic. The level of carcinogenicity may vary widely between different members of this group. Minor constituents of PAH mixtures may make large contributions to the carcinogenic activity of the mixture. Certain methylchrysenes, particularly the 5-isomer, which is one of the most carcinogenic compounds known, may dominate the carcinogenic activity of a mixture (Bartle 1991).

Rhee and Bratzler (1968) analyzed hydrocarbons in smoke, and the amounts found in smoke and in the vapor phase (smoke filtered to remove particles) are listed in Table 15.18. Small amounts of these smoke constituents may be transferred to

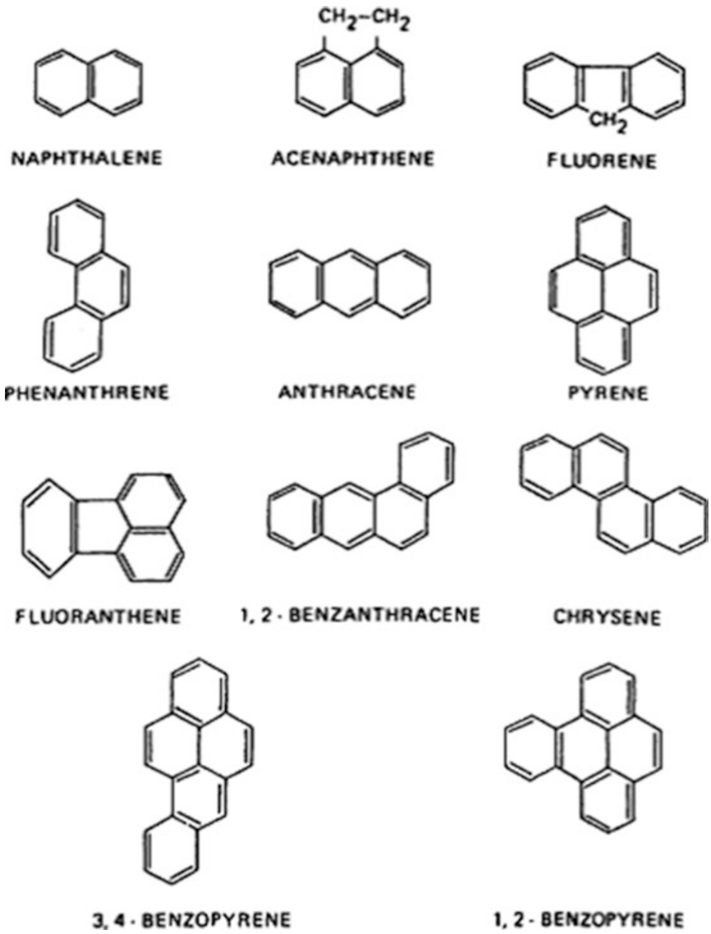


Fig. 15.15 Chemical structure of some polycyclic aromatic hydrocarbons

Table 15.18 Aromatic polycyclic hydrocarbons in wood smoke and in wood smoke vapor phase

Hydrocarbon	Amount, µg/45 kg sawdust	
	whole smoke	vapor phase
Phenanthrene	51.5	28.4
Anthracene	3.8	1.9
Pyrene	5.5	4.1
Fluoranthene	5.7	4.2
1,2-Benzanthracene	7.0	4.3
Chrysene	2.6	0.3
3,4-Benzopyrene	1.2	0.4
1,2-Benzopyrene	0.9	Trace

Source: From K.S. Rhee and L.J. Bratzler, Polycyclic Hydrocarbon Composition of Wood Smoke, *J. Food Sci.*, Vol. 33, pp. 626–632, 1968

foods during smoking. Howard and Fazio (1969) reported the levels of aromatic polycyclic hydrocarbons in foods, and results for smoked foods are listed in Table 15.19. These compounds have also been found in unsmoked foods, as is shown in Table 15.20. Higher levels than those found in smoked food may occur as a result of barbecuing or charcoal broiling. Roasting of coffee and nuts results in formation of PAHs. The levels present in roasted coffee increase with more intense roasting; this is shown in Table 15.21, which is based on results obtained by Fritz (1968). PAHs occur in vegetables (Grimmer and Hildebrand 1965), and the levels are thought to be related to the leaf area and the relative level of atmospheric pollution.

Surprisingly, the largest proportion of the total human intake of PAHs does not come from smoked or roasted foods, but from other common products. Bartle (1991) has stated that cereals are likely to be a greater hazard, especially in the

Table 15.19 Polycyclic aromatic hydrocarbons found in smoked food products (ppb)

Food Product	Benzo (a)-anthracene	Benzo (a)-pyrene	Benzo (e)-pyrene	Benzo (g,h,i,)-perylene	Fluoranthene	Pyrene	4-Methyl-pyrene
Beef, chipped	0.4				0.6	0.5	
Cheese, Gouda					2.8	2.6	
Fish							
Herring					3.0	2.2	
Herring (dried)	1.7	1.0	1.2	1.0	1.8	1.8	
Salmon	0.5		0.4		3.2	2.0	
Sturgeon		0.8			2.4	4.4	
White					4.6	4.0	
Ham	2.8	3.2	1.2	1.4	14.0	11.2	2.0
Frankfurters					6.4	3.8	
Pork roll					3.1	2.5	

Source: From J.W. Howard and T. Fazio, A Review of Polycyclic Aromatic Hydrocarbons in Foods, *Agr. Food Chem.,* Vol. 17, pp. 527–531, 1969, American Chemical Society

Table 15.20 Polycyclic aromatic hydrocarbons in unsmoked food products

Food Product	Fluoranthene (ppb)	Pyrene (PPb)
Cheese, cheddar	0.8	0.7
Fish, haddock	1.6	0.8
Fish, herring (salted)	0.8	1.0
Fish, salmon (canned)	1.8	1.4

Source: From J.W. Howard and T. Fazio, A Review of Polycyclic Aromatic Hydrocarbons in Foods, *Agr. Food Chem.,* Vol. 17, pp. 527–531, 1969, American Chemical Society

Table 15.21 Polycyclic Aromatic Hydrocarbons in Coffee (μg/kg)

Compound	Heavy roasting	Normal roasting
Anthracene	6.2	1.5
Phenanthrene	74.0	28.0
Pyrene	28.0	3.5
Fluoranthene	34.0	3.9
1,2-Benzanthracene	14.2	1.5
Chrysene	14.8	–
3,4-Benzopyrene	5.8	0.3
1,2-Benzopyrene	7.0	0.7
Perylene	0.6	–
11, 12-Benzfluoranthene	1.8	–
Anthanthrene	0.9	–
1, 12-Benzperylene	2.2	–
3,4-Benzfluoranthene	1.2	–
Coronene	0.9	–
Indenopyrene	0.7	–

Source: From W. Fritz, Formation of Carcinogenic Hydrocarbons During Thermal Treatment of Foods, *Nahrung,* Vol. 12, pp. 799–804, 1968

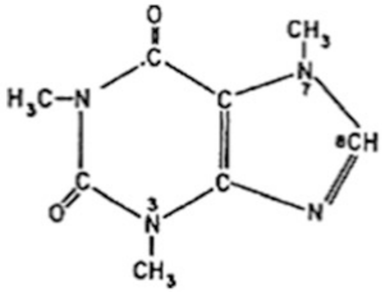


Fig. 15.16 The structure of caffeine 1,3,7- trimethylxanthine

form of flour, than smoked or barbecued foods. Although cereal has a much lower PAH content than smoked or roasted foods do, cereal is consumed in much greater amounts.

Caffeine

Caffeine is a naturally occurring chemical, 1,3,7-trimethylxanthine (Fig. 15.16), which is found in the leaves, seeds, and fruits of more than 63 species of plants growing all over the world. It occurs as a constituent of coffee, tea, cocoa, and chocolate, and is an additive in soft drinks and other foods. Because humans have used it for thousands of years, caffeine has GRAS status in the United States. Roberts and Barone (1983) have estimated that daily caffeine consumption in the United States is 206 mg per person. Caffeine shows a number of physiological effects (Von Borstel 1983) and, as a result, its regulatory status has been under review (Miles 1983). Complicating the matter is the fact that caffeine is both a naturally occurring chemical as well as a food additive. Caffeine stimulates the central nervous system, can help people stay awake, and can relieve headaches. Adverse effects may include sleep disturbance, depression, and stomach upsets. Large overdoses of caffeine may be fatal (Leviton 1983). Caffeine is a good example of a widely occurring natural toxicant that has been part of our food supply for centuries.

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