



Online Training Curriculum

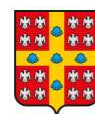
Confirmation Methods for Food contaminants

General Background on food contaminants and food regulatory management

Introduction to Food contaminants as a food hazard

Jérémie Théolier, Ph.D.

Research Associate, Laval University



UNIVERSITÉ
LAVAL

Faculty of Agriculture
and Food Sciences

Overview

What are food contaminants?.....	1
Proposed Classification of Food Contaminants	1
Naturally occurring contaminants.....	1
Agrochemicals	6
Environmental contaminants	8
Food-Processing-Induced Chemicals	11
Necessity to control the levels of chemical contaminants in food	13
References	14

What are food contaminants?

The Codex Alimentarius Commission defines a contaminant as follows:

“Any substance not intentionally added to food or feed for food producing animals, which is present in such food or feed as a result of the production (including operations carried out in crop husbandry, animal husbandry and veterinary medicine), manufacture, processing, preparation, treatment, packing, packaging, transport or holding of such food or feed, or as a result of environmental contamination. The term does not include insect fragments, rodent hairs and other extraneous matter (also regrouped under the term physical hazards)” [1].

Thus, food contamination refers to the presence of harmful chemicals and microorganisms in food, which may cause consumer illness. Food contaminants typically include environmental contaminants, food processing contaminants, unapproved adulterants and food additives, and chemicals resulting from the migration from packaging materials [2]. The impact of chemical contaminants on consumer's health and well-being can manifest in the form of acute health effects or, become apparent only after many years of prolonged exposure to such contaminants at low levels.

Proposed Classification of Food Contaminants

Food contaminants are often classified according to the source of contamination and the mechanism by which the contaminants may enter the food supply.

Naturally occurring contaminants

This category includes the **Naturally occurring contaminants/toxicants**: which are chemicals that are produced under specific conditions by living organisms. Mycotoxins, phycotoxins and other

compounds are included in this grouping. The production of some contaminants may be influenced by human activity, which can contribute to an increase of their availability and occurrence in food products [3].

- **Mycotoxins**

Mycotoxins are toxic secondary metabolites that are naturally produced by certain types of fungi and that are associated with health disorders in animal and human beings. Most mycotoxins are chemically stable and survive food processing contrary to bacterial toxins. The lack of visible appearance of fungus on a given food crop does not negate the presence of mycotoxins as they can remain on the food products after the fungus has been eliminated.

Several hundred different mycotoxins have been identified, but the most commonly observed mycotoxins in food and feed, which present a concern for human health and livestock include:

- aflatoxins,
- ochratoxin A,
- patulin,
- fumonisins,
- zearalenone and
- nivalenol/deoxynivalenol.

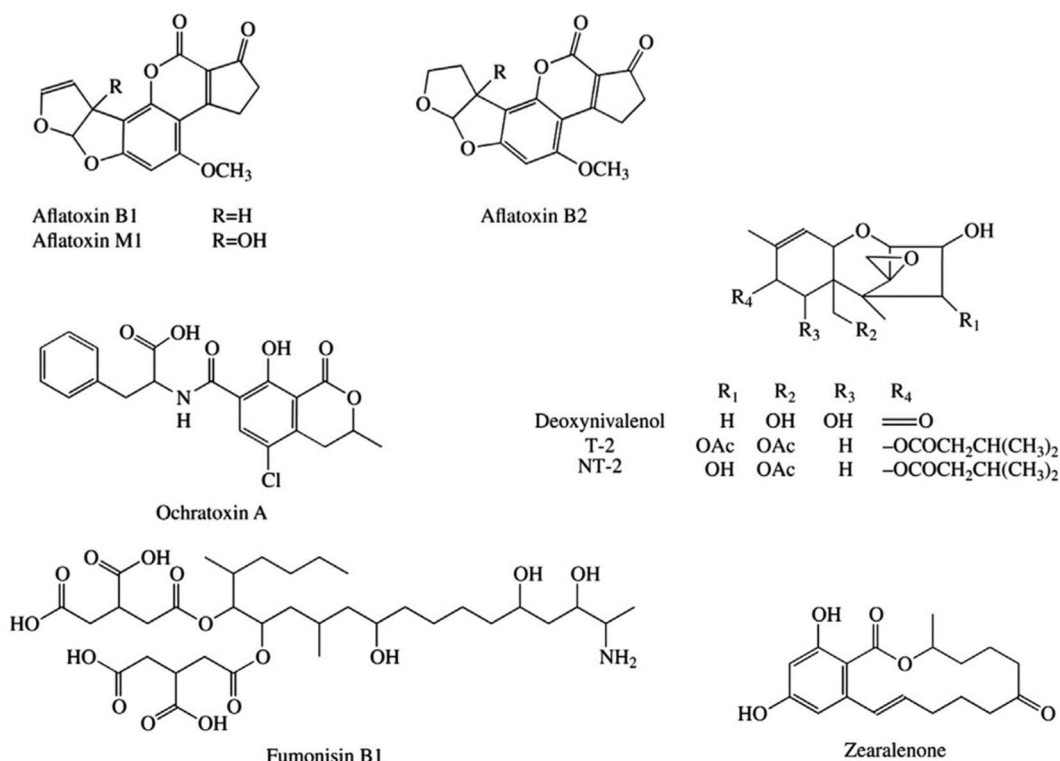


Figure 1: Molecular structures of the main mycotoxins. From Vidal et al. (2009) [4]

The production of mycotoxins depends on the surrounding intrinsic and extrinsic environments and these substances vary greatly in their toxicity, depending on the organism infected and its susceptibility, metabolism, and defense mechanisms. Mycotoxins appear in the food chain as a result of molds infection of crops both before and after harvest. The contamination can occur either before harvest or after harvest, during storage, on/in the food itself often under warm, damp and humid conditions. Consequently, mycotoxins can be found on numerous foodstuffs such as cereals, dried fruits, nuts and spices. Exposure to mycotoxins can happen either directly by eating infected food or indirectly from animals that are fed contaminated feed, which may lead to the occurrence of such toxins in food of animal origin and in particular from milk.

The presence of mycotoxins in food and / or feed can have major consequences, making the products unfit for consumption. Depending on the ingested doses, mycotoxins have the potential to lead to both acute and chronic health effects. For this reason, mycotoxins have to be monitored to prevent unsafe products from reaching consumers. The Codex Alimentarius Commission (Codex), the international food standard setting body, developed over the past years several standards and guidelines to help control these contaminants, in the form of maximum levels not to be exceeded in

foods/ feed ingredients produced or sold as well as codes of practice, offering guidance as to how to prevent and mitigate the growth and activity of the culprit micro-organisms [1,5].

- **Phycotoxins**

Phycotoxins are complex chemicals produced by eukaryotic and prokaryotic algal organisms. Like mycotoxins, phycotoxins are secondary metabolites. These metabolites may be toxic to other living organisms, including humans. They will bioaccumulate in tissues when ingested by higher trophic animals all along the food chain. They are odorless, tasteless and need specific analytical methods to be detected. Besides, these compounds can undergo modifications all along the food chain which complicates their identification/quantification [3].

Major phycotoxins are:

- Domoic acid that causes amnesic shellfish poisoning (ASP)
- Saxitoxins, causing the paralytic shellfish poisoning (PSP)
- Okadaic acid, one of the primary causes of diarrhetic shellfish poisoning (DSP)
- Ciguatoxins, causing ciguatera, is present in tropical waters
- Brevitoxins, maitotoxins, etc...

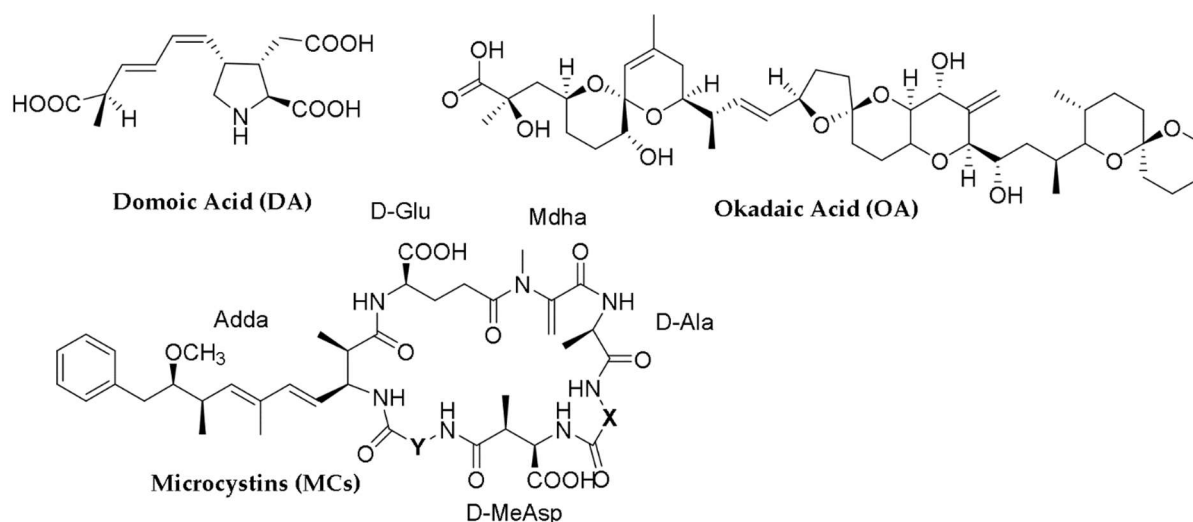


Figure 2: Molecular structure of Domoic Acid, Okadaic Acid and Microcystins. From Merlo et al. (2020) [6]

- **Phytotoxins**

Phytotoxins are toxic chemicals produced by plants, which function as defensive agents against their predators.

Main phytotoxins are:

- Toxic phenolic compounds (tannins, flavonoids, etc..)
- Toxic alkaloids (for example solanine in potatoes). They often have a bitter taste.

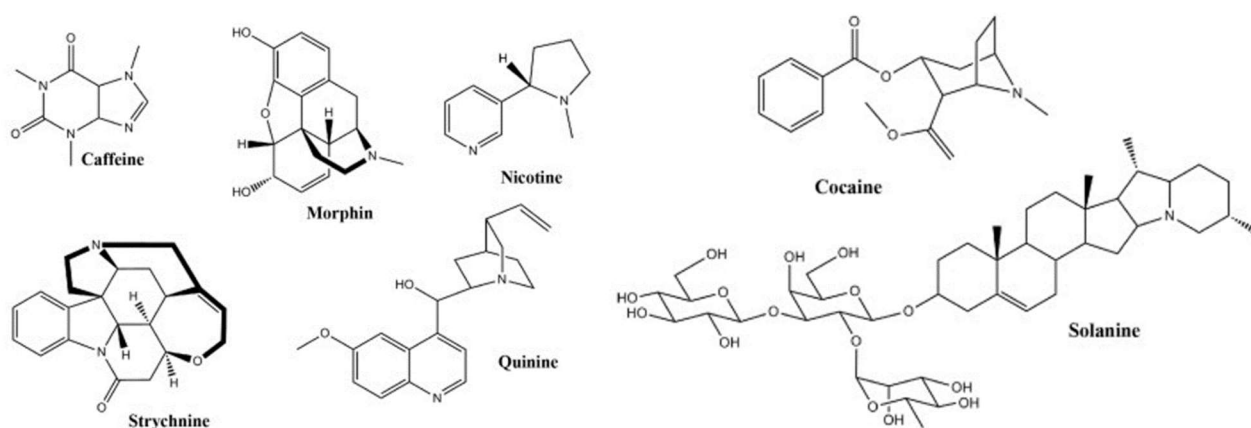


Figure 3: Molecular structure of toxic alkaloids. From Murphy (2017)

- Cyanogenic compounds that will produce cyanides that are highly toxic for humans.

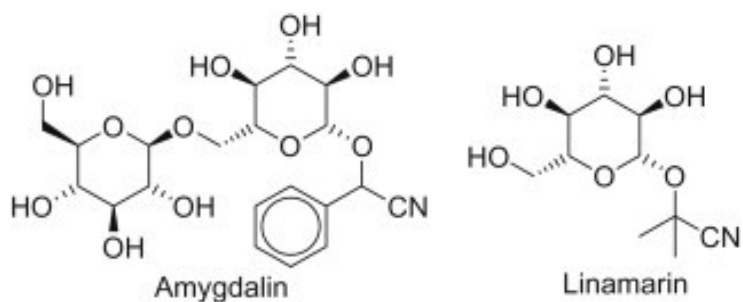


Figure 4: Molecular structure of Cyanogenic compounds. From Dusemond et al. (2017)

Cassava, sorghum, stone fruits, bamboo roots and almonds are especially important foods containing cyanogenic glycosides. The potential toxicity of a cyanogenic plant depends primarily on the potential that its consumption will produce a concentration of cyanide that is toxic to humans, when exposed.

Finally, wild mushrooms may contain several toxins which can cause vomiting, diarrhoea, confusion, visual disturbances, salivation, and hallucinations. These toxins are also considered as phytotoxins. Fatal poisoning is usually associated with delayed onset of symptoms which are very severe, with toxic effect on the liver, kidney and nervous systems. Cooking or peeling does not inactivate the toxins. It is recommended to avoid any wild mushrooms, unless definitively identified as non-poisonous.

It is unlikely that humans consume fatal doses of phytotoxins. For this reason, they are rarely monitored by regulatory agencies but phytotoxins can still be the cause of food poisoning.

- **Animal toxins**

Few animal toxins are involved in foodborne poisoning. In fact, food poisoning involving animals are often linked to microbial contamination. However, animals and animal food stuffs can be the carrier of several toxic compounds produced at lower trophic level in the food chain. For example, milk and eggs can be the carrier of mycotoxins and fish can present high concentration of phycotoxins as well as shellfish. Some venomous animals are eaten after the removal of venomous gland (Pufferfish, snakes, scorpions, etc.). All those molecules are not monitored by regulatory agencies.

Agrochemicals

Agrochemicals are chemicals used in agricultural practices and animal husbandry with the intent to increase yields of crops and animal derived foods. Such agents include pesticides and veterinary drugs.

A **pesticide** is a chemical substance designed to be effective against pests. The common terminology refers to plant protection products. Plant protection products are mainly applied on crops to keep them healthy and to prevent them from being destroyed by disease and infestation. They include herbicides, fungicides, insecticides, acaricides, plant growth regulators and repellents. However, this terminology (pesticide) also covers products such as biocides, which are intended for non-plant uses to control pests and disease carriers such as insects, rats and mice. Indeed, there are many different

types of pesticides; each is meant to be effective against specific pests. The current understanding of the pesticide terminology includes amongst others [7,8,9]

- Algaecides designed to kill and/or slow the growth of algae.
- Antimicrobials designed to control germs and microbes such as bacteria and viruses.
- Disinfectants also designed to control germs and microbes such as bacteria and viruses.
- Fungicides designed to control fungal problems like molds, mildew, and rust.
- Herbicides designed to kill or inhibit the growth of unwanted plants, also known as weeds.
- Insecticides designed to control insects.
- Acaricides designed to control acari species
- Nematicides designed to control nematodes
- Molluscicides designed to manage molluscs
- Insect Growth Regulators designed to disrupt the growth and reproduction of insects.
- Rodenticides designed to kills rodents like mice, rats, and gophers.
- Wood Preservatives aimed to make wood resistant to insects, fungus and other pests.

Pesticides can also be classified by chemical structure (e.g., organic, inorganic, synthetic, or biological), or physical state (e.g. gaseous (fumigant)).

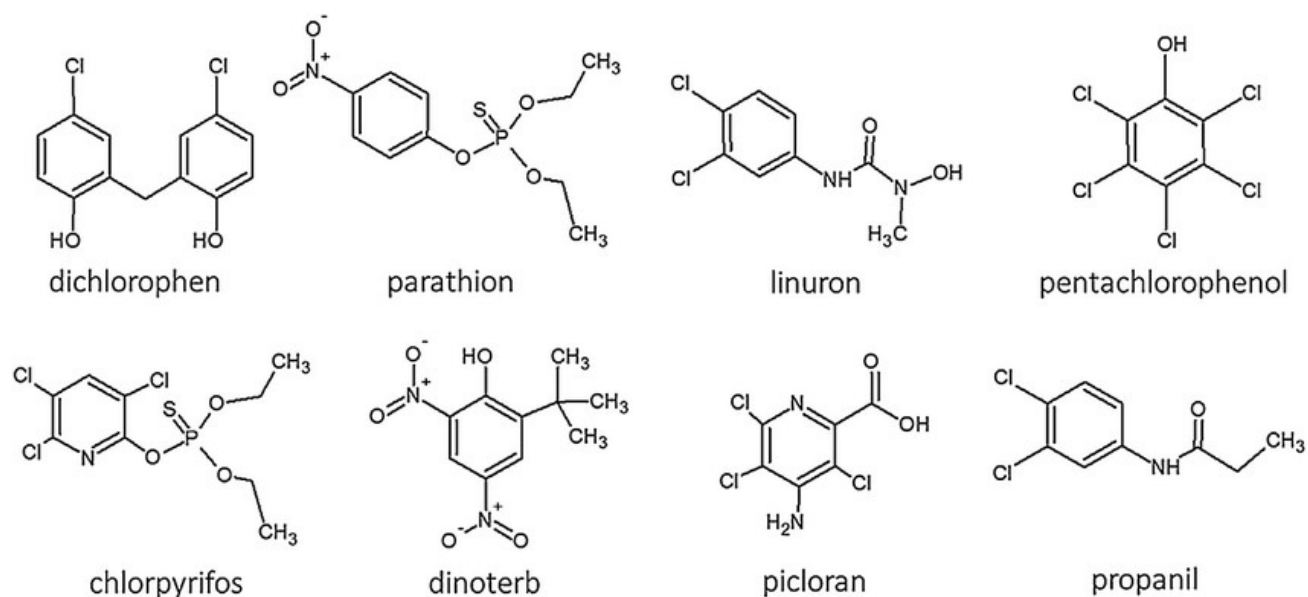


Figure 5: Molecular structure of pesticides. From Alejo-González et al. (2017) [10]

A **veterinary drug** (also animal drug) refers to a drug intended for use in the diagnosis, cure, mitigation, treatment, or prevention of disease in animals. Like for pesticides, residues of veterinary drugs may pose health risks when consumed through food.

Exposure of the general population to these molecules most commonly occurs through consumption of treated food sources or being in close contact to areas treated with pesticides such as farms or lawns. Other exposure sources are related to occupational activities, such as pesticide spraying in farming practices.

Pesticides and Veterinary drugs are subjected to approval by regulatory bodies. The assessment of safe conditions of use, including exposure to low level residues of these substances is part of this assessment. The regulatory management of these substances in conjunction with food production, includes the development of Maximum Residue Limits, which limits of occurrence of residues of these substances and their metabolites (where relevant), not to be exceeded in food and/or feed.

Environmental contaminants

Environmental contaminants are chemicals that accidentally or deliberately enter the environment, often, but not always, as a result of human activities. Some of these contaminants may have been manufactured for industrial use and because they are very stable, they do not break down easily. If released to the environment, these contaminants may enter the food chain [11].

A wide variety of environmental contaminants have been detected in foods. These range from metals and "ionic" species like perchlorate to organic (carbon-based) substances, including the so-called "persistent organic pollutants". **Persistent organic pollutants (POPs)** are chemicals of global concern due to their potential for long-range transport, persistence in the environment, ability to bio-magnify and bio-accumulate in ecosystems, as well as their significant negative effects on human health and the environment. Some of the POPs are agrochemicals that are now banned (like DDT).

Other environmental contaminants are **naturally occurring chemicals**, but industrial activity may increase their mobility or increase the amount available to circulate in the environment, allowing them to enter the food chain at higher levels than would otherwise occur.

In reviewing the series of POPs several molecules are listed:

- **Dioxins and furans**

Dioxins and furans are the common names for a group of chemicals that are formed during combustion processes such as waste incineration, power generation, metal production, and fuel burning.

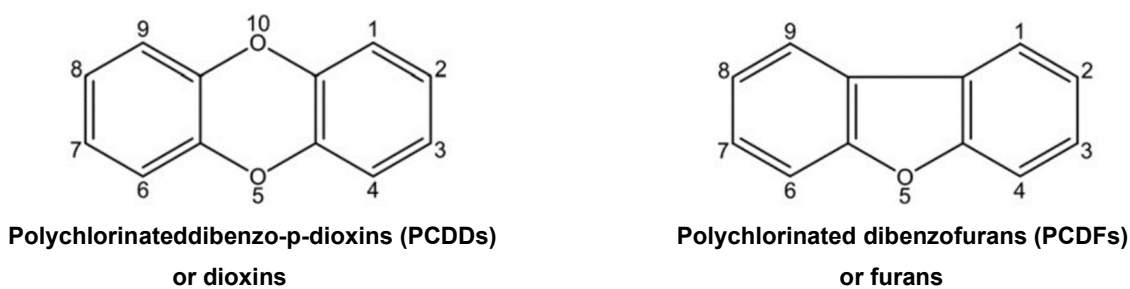


Figure 6: Molecular structure of dioxins and furans. Adapted from Loganathan & Masunaga (2009) [12]

- **Polychlorinated biphenyls (PCBs)**

Polychlorinated biphenyls were once widely deployed as dielectric and coolant fluids in electrical apparatus, carbonless copy paper and in heat transfer fluids. The bromine analogues of PCBs are polybrominated biphenyls (PBBs), which have analogous applications and environmental concerns. They are banned since 2001 by the Stockholm Convention on Persistent Organic Pollutants.

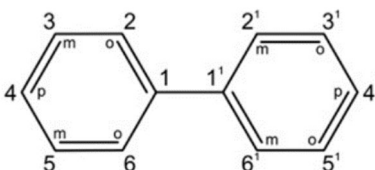


Figure 7: Molecular structure of PCBs. Adapted from Loganathan & Masunaga (2009) [12]

- **Polybrominated Diphenyl Ethers (PBDEs)**

PBDEs are commercially produced substances that are used as flame retardants in a wide variety of consumer products.

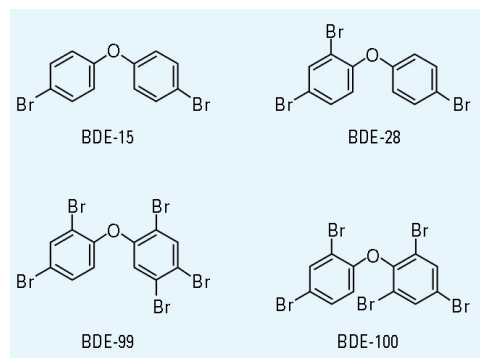


Figure 8: Molecular structure of 4 PBDEs congeners. From Kojima et al. (2009) [13]

- **Perfluorinated chemicals (PFCs)**

PFCs are man-made chemicals that are used in commercial and consumer products and that also have a variety of industrial applications. Perfluorooctane sulfonate (PFOS) is perhaps the most well-known PFC and has been used, amongst other things, as a water, stain, and oil repellent for textiles, carpet, and food packaging, a surfactant in the electroplating industry, and an additive in fire fighting foams.

Among the chemicals of possible “natural environmental presence”, potentially exacerbated by human activity:

- **Perchlorate**

Perchlorate (ClO_4^-) is an inorganic compound that occurs naturally in nitrate deposits and potash ore. It may also be present in air, soil, and water as a result of the industrial uses of perchlorate salts (perchlorate combined with another element or compound such as sodium or ammonium) and nitrate fertilizers. Perchlorate salts are primarily used in solid fuels, explosives, fireworks, road flares, air bag inflators, rubber manufacturing, paint and enamel manufacturing and pulp and paper processing. Perchlorates may contaminate food and water as result of human activity such as production and storage of explosives, fireworks, fuels etc.. Such contamination generally affects soils and aquifers.

- **Heavy metals**

Lead is a naturally occurring metal found in rock and soil that also has many industrial applications. Lead can enter the food chain through various pathways. For example, plants uptake lead from the soil and airborne lead may also be deposited on their surfaces. Also, fish can absorb lead from water

and sediments while other animals may be exposed to lead through the foods they eat. Lead may also be introduced to foods from the use of lead containing dishware such as lead glazed pottery or lead crystalware. The preparation of foods with water containing lead can also introduce lead to foods.

Arsenic is a naturally occurring chemical element found throughout our environment and its living systems. Arsenic can enter groundwater through erosion and weathering of soils, minerals, and ores. Arsenic compounds are used in the manufacture of a variety of products and may enter our environment directly from industrial effluents and indirectly from atmospheric deposition. Arsenic can be found at very low levels (low parts per billion (ppb)) in many foods, including meat and poultry, milk and dairy products, bakery goods and cereals, vegetables, and fruits and fruit juices. The trace levels of arsenic in foods generally reflect normal accumulation from the environment.

Mercury is a naturally occurring metal in soil, rocks, and water bodies. It can also be released into the environment as a result of human activities involving combustion processes such as coal-fired power generation, metal mining, and waste incineration. The most common source of human exposure to mercury is the consumption of certain types of fish, primarily predatory fish. Others heavy metals like cadmium, antimony or tin can also be found in foodstuffs and should be monitored when needed.

Food-Processing-Induced Chemicals

Some chemicals can be formed in certain foods during processing as a result of reactions between compounds that are natural components of the food. In some cases, such chemicals may be formed as a result of a food additive being intentionally added to food and reacting with another compound in the food. When foods are heat-processed (baked, deep-fried, etc.), there are reactions that occur between components of the food, resulting in the desired flavour, appearance and texture of the food. However, some of these reactions can lead to the production of such compounds. Similarly, certain storage or processing conditions may allow reactions to occur that otherwise would not. These reactions could generate potentially harmful compounds. These chemicals are collectively referred to as food-processing-induced chemicals. Some of these chemical reactions involve naturally occurring components in the food, while other reactions may involve food additives, ingredients, or food packaging materials that were intentionally used [14].

In many cases, the presence of processing-induced chemicals in food cannot be avoided; however, understanding the processes by which these products are formed can allow us to optimize or adjust food preparation methods, formulae or processes, thereby reducing or eliminating the formation of such chemicals.

Examples of food-processing induced chemicals include:

- **Acrylamide**

Acrylamide is a chemical that naturally forms in certain foods, particularly plant-based foods that are rich in carbohydrates and low in protein, during processing or cooking at high temperatures, through a reaction known as the Maillard Reaction. The highest concentrations of acrylamide have been detected in potato chips and French fries, although it has been found in other foods as well. Additional research is being undertaken in order to more fully understand the risks of acrylamide exposure through food sources to humans.

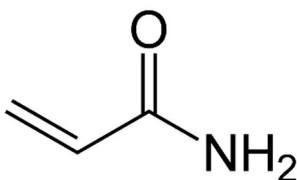


Figure 9: Chemical structure of acrylamide

- **Benzene**

Benzene is a known human carcinogen. It is naturally occurring but is also manufactured for use in the industrial sector. We are exposed to benzene mainly through inhalation (e.g., vehicle exhaust and cigarette smoke) and to a much lesser extent through the ingestion of food and water. Trace amounts of benzene can form in beverages when ascorbic acid (Vitamin C) combines with either sodium benzoate or potassium benzoate. Benzoates are common preservatives sometimes added to beverages to prevent bacterial growth.

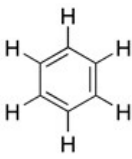


Figure 10: Chemical structure of Benzene

Other food-processing-induced chemicals include:

- Chloropropanols
- Ethanol
- Ethyl carbamate
- Furan
- Heterocyclic aromatic hydrocarbons
- Nitrosamines
- Polycyclic aromatic hydrocarbons (PAH's)
- Semicarbazide

Necessity to control the levels of chemical contaminants in food

Several health issues (including cancer, neurodevelopmental disorder and reproductive disorder) have been associated with exposure to food contaminants. All these compounds may have acute or delayed health effects in humans. Several methods of prevention of the introduction and possible accumulation of contaminants in food, have been developed and applied, primarily, in the form of codes of practice made of interventions that ensure these chemicals are avoided or eliminated throughout the food production process. Regulatory measures were also developed as an additional approach for the management of these substances in food and feed. Some of these measures include the set-up of maximum values: Maximum Limits (MLs) or Maximum Residue Limits (MRLs) of specific chemical substances, not to be exceeded in certain food and/or feed. These values support the food production sector by having a systematic approach to be applied by industry to ensure compliance. Food monitoring activities, to measure chemicals in food on a regular basis, coupled by risk assessment enable food competent authorities to ascertain that levels of chemicals present in food do not pose undue risks to human health for a given population [15].

References

1. Codex Alimentarius. (2019) CXS 193-1995. General standard for contaminants and toxins in food and feed. Available at: <http://www.fao.org/fao-who-codexalimentarius/thematic-areas/contaminants/en/>
2. Rather et al. (2017). The Sources of chemical contaminants in food and their health implications. *Frontiers in Pharmacology*, 8: article 830.
3. Health Canada. Available at: <https://www.canada.ca/en/health-canada/services/food-nutrition/food-safety/chemical-contaminants/natural-toxins.html>
4. Vidal et al. (2009). Use of polyclonal antibodies to ochratoxin A with a quartz-crystal microbalance for developing real-time mycotoxin piezoelectric immunosensors. *Analytical and Bioanalytical Chemistry*, 394(2):575-582.
5. Codex Alimentarius. (2017) CXC 78-2017. Code of practice for the prevention and reduction of mycotoxins in spices. Available at: <http://www.fao.org/fao-who-codexalimentarius/thematic-areas/contaminants/en/>
6. Merlo et al. (2020). Simultaneous pre-concentration and HPLC-MS/MS quantification of phycotoxins and cyanotoxins in inland and coastal waters. *International Journal of Environmental Research and Public Health*, 17: 4782.
7. United States Environmental Protection Agency. Available at: <https://www.epa.gov/safepestcontrol/why-we-use-pesticides>
8. European Commission. Available at: https://ec.europa.eu/food/plant/pesticides_en
9. Codex Alimentarius. Available at: <http://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/functional-classes/en/>
10. Alejo-González et al. (2017). PEGylation of cytochrome P450 enhances its biocatalytic performance for pesticide transformation. *International Journal of Biological Macromolecules*, 105: 163–170.

11. Health Canada. Available at: <https://www.canada.ca/en/health-canada/services/food-nutrition/food-safety/chemical-contaminants/environmental-contaminants.html>
12. Loganathan & Masunaga (2020). PCBs, dioxins and furans: Human exposure and health effects. In Handbook of Toxicology of Chemical Warfare Agents (Third Edition) – Chapter 18: 267-278.
13. Kojima et al. (2009). Nuclear hormone receptor activity of Polybrominated Diphenyl Ethers and their hydroxylated and methoxylated metabolites in transactivation assays using Chinese hamster ovary cells. Environmental Health Perspectives, 117(8): 1210-1218.
14. Health Canada. Available at: <https://www.canada.ca/en/health-canada/services/food-nutrition/food-safety/chemical-contaminants/food-processing-induced-chemicals.html>
15. Health Canada. Available at: <https://www.canada.ca/en/health-canada/services/food-nutrition/food-safety/chemical-contaminants/maximum-levels-chemical-contaminants-foods.html>