Trace Metals and Food Risks

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Abstract Contamination of food by metal residues remains in the forefront of food security concerns worldwide. The presence of these trace elements in fruits, vegetables, cereals, meats, fish, seafood, shellfish, eggs and milk is the subject of several monitoring plans.

Living beings can be contaminated by these trace metals through their presence in the environment or through the consumption of polluted water and food.

The accumulation of these metals in the living organisms can have harmful effects depending on the type of toxicity.

In this chapter entitled "Trace Metals and Food Risk", we will focus on the exposure routes of the population to trace metals and the negative effects associated with chronical contamination by the latter.

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1 Introduction

In the last few decades, the presence of toxic contaminants in food and water has caused increasing concern from public opinion and health organizations worldwide. Anthropic activities and industrialization in particular contributed to a significant increase in pollutants, which led to an accumulation of contaminants in the food chain. The presence of these toxic elements in the environment and foodstuff at relatively high concentrations can have detrimental effects on the environment and human health.

Food contamination refers to the presence of pathogenic microorganisms in food and also to the harmful chemicals and metals used in agricultural and livestock breeding practices to increase production. Unlike foodborne pathogens, chemical and metallic contaminants in food are often not removed by cleaning and heat treatment. Chemical and metallic contaminants can be classified according to the source of contamination and the mechanism by which they penetrate into the food product.

The contaminants under scrutiny are closely associated with proven as well as potential critical effects on humans. Three categories of contaminants are monitored: environmental contaminants, those associated with inputs used in animal breeding and agriculture, and those associated with a lack of adequate hygiene control over food processing operations. These hazardous contaminants could highly be codified according to the source of contamination and the process through which they enter the food product.

Among these contaminants, heavy metals are increasingly observed in animal source foods (fish and seafood) and plant-based food (fruit, vegetables, and cereals). These metals are naturally omnipresent in surface water; however, their concentrations are generally very low, which explains their denominations as "trace metals" or "metallic trace elements." In addition, they are also produced by anthropic activities, notably industrial and mining activities.

According to a study published in 2015 on food alerts and collective food poisoning as far as food chain monitoring is concerned, the MUS received 952 alerts in France. The distribution of alerts by type of product places meat products at the top of the ranking (40.76%), followed by fishery products (22.58%) and dairy products (17.33%). According to the same study, the five contaminants most frequently associated with product alerts are *Listeria monocytogenes* (32%), followed by *Salmonella* (16%) and heavy metals (9.1%). Additionally, the consumption of fruits and vegetables plays a crucial role in a diversified and nutritious diet. The World Health Organization recommends that we should consume a minimum of 400 g of fruits and vegetables a day to reduce the risk of serious health problems, such as heart disease, stroke, other certain types of cancer, etc.

However, these fresh fruits and vegetables can nevertheless be exposed to contaminants before being consumed. Several epidemiological studies have classified raw fruits and vegetables as the second source of foodborne illness. The consumption of vegetables contaminated with heavy metals can lead to serious human health problems.

Food contains a broad spectrum of metallic elements that are essential in trace amounts for cell functions maintenance at biological, chemical, and molecular levels. Other heavy metals have no functional effects on the body and can be harmful to health if foodstuffs containing them are consumed regularly. The majority of metals are natural components of the Earth's crust (Madkour 2020). Metals and other elements can be naturally present in food or can enter food as a result of human activities such as industrial and agricultural processes (FSAI 2009).

The aim of this chapter is to provide a concise overview of the health hazards due to food metallic contamination. This chapter will deal with mercury, lead, and cadmium.

2 Basic Reminders

Heavy metals are elements having atomic weight between 63.546 and 200.590 and a specific gravity greater than 4.0. They are ubiquitous in the environment; however, their concentrations are generally extremely low, which explains their actual designations of "trace metals" or "trace elements (TEs)."

In contrast to the vast majority of organic contaminants, heavy metals are constituents natural in rocks and mineral deposits. So normally these elements are present at low levels (less than 0.1%) in soils, sediments, surface water, and living organisms (Alloway and Ayres 1997; Callender 2003).

Due to their different specific characteristics, heavy metals are widely used in the field of metallurgy and electronics. As a result, their anthropogenic sources are vast and their introduction into the environment is fairly recent (Callender 2003).

The main anthropogenic source of heavy metals for the environment is that produced by the mining activity and in associated industries, and it has also been identified as one of the first man-made environmental impacts (Nriagu 1996). In addition, the metallurgical industry, fertilizers and pesticides applied in soil cultivation, household waste incinerators, medical waste, emissions from factories, and sewage effluents are also considered anthropogenic sources of heavy metals (Cotran et al. 1990).

The nonbiological essential heavy metals of particular concern in relation to harmful effects on health include mercury (Hg), lead (Pb), cadmium (Cd), tin (Sn), and arsenic (As). Heavy metals can contaminate the ecosystem with industrial waste and acidic rain. Once these heavy metals are bioavailable in the ecosystem, they readily contaminate various foods and subsequently are ingested by living organisms. Heavy metal poisoning could result from drinking water contamination, intake via the food chain, or through the breathing of air contaminated by emission sources of heavy metals.

Some heavy metals are essential trace elements, with functions that are very essential to various biological processes, driving the entire human metabolism. Some heavy metals are essential trace elements, with functions that are very essential to various biological processes, driving the entire human metabolism. Among these elements, some are indispensable, whose absence hinders the functioning or could even prevent the development of an organism. For example, iron (Fe), manganese (Mn), zinc (Zn), and copper (Cu) for plants and animals. In addition, cobalt (Co), chromium (Cr), and selenium (Se) are essential only for animals, while molybdenum (Mo) is a micronutrient for plants (Alloway and Ayres 1997).

3 Routes of Exposure

Most heavy metals are toxic and enter the environment primarily as a consequence of industrial emissions or via disposal of products containing these metals. Soil, water, food, and air are the major exposure media for humans and others living organisms.

3.1 Exposure Through Soil

The heavy metals present in soils are derived from the geochemical reserve, on the one hand, and from the cumulation of anthropogenic inputs, on the other. Soil as a nonrenewable resource, serving as an interface between air and water, is currently faced with complex pollution generated by several human activities, including fertilizing materials, pesticides, and the dumping of wastes and sewage sludge, which involves significant contributions to increasing the concentration of metals in the environment (Granero and Domingo 2002).

Metals can be either fixed in rocks and sediments or mobile. In the first case, the quantities available are extremely small and have no significant effect on the environment. When environmental conditions change in such a way that metals become soluble, the increase in concentration then becomes a direct threat to the environment due to the increase in their availability to living beings. Furthermore, acid rain can increase the mobility of metallic elements in the pores soil by changing its buffer capacity, causing an elevation of their concentrations in agricultural products their concentration in agricultural products**.** Three important origins can thus be distinguished: geochemical background (natural background levels), atmospheric deposition, and anthropogenic inputs (Perrono 1999).

3.2 Geochemical Background

Naturally, the soil contains heavy metals from the bedrock in which it was formed. Thus, soils formed on quartz sands contain extremely low amounts of metals (less than 0.05 mg/kg DM of Cd, less than 5 mg/kg DM of Cu), whereas those formed on calcareous or marly sediments or shales are richer (0.5–1 mg/kg DM of Cd, 25–50 mg/kg DM of Cu) (Perrono 1999). On the basis of a study of 333 soils samples conducted by Pallier, the Ni content of soils is particularly high when the soils have developed on marly or calcareous bedrock (Pailler 1992).

Sedimentary rocks have fairly high levels of trace elements, which increase in the event of fossil carbon accumulation. Notwithstanding this relative abundance in calcareous soils, trace elements are relatively mobile due to the high pH of this type of soil.

3.3 Atmospheric Deposition

The impact of atmospheric pollution on the environment, including atmospheric deposition, is a major concern worldwide. Air pollutants can be emitted in many forms, and their levels of toxicity also vary considerably.

Trace elements eventually deposit on the ground surface depending on wind patterns and ultimately increase their concentrations in adjacent areas.

Atmospheric deposition of these trace elements increases their concentrations in soil and consequently in the food chain (Sharma et al. 2008). The majority of these trace metals are not biodegradable and have effects on food safety (Lim et al. 2005). Heavy metals are released into the atmosphere, usually from anthropogenic sources, including road components, traffic, power plants, industries, and residential heating. To this anthropogenic fallout be added a natural level related to wind erosion of soils and volcanic eruptions.

4 Anthropogenic Inputs

The quasi-totality of the anthropogenic inputs of trace metals is due to the massive use of fertilizer materials, pesticides, and the land application of waste and sludge, and the concentration of heavy metals in soils can increase by repeated and excessive fertilizer and pesticide applications.

4.1 The Fertilizer Materials

These include primary macronutrients, secondary macronutrients, micronutrients, and mixtures thereof. Some types of fertilizers obtained by processing products from mineral deposits contain metal elements that are often much higher than those of the majority of soils. So, the phosphate deposits used in the manufacture of fertilizers are often quite loaded with heavy metals (Perrono 1999). This is notably the case for cadmium, in which the phosphorus content is 70–100% of the metal initially present in the ore (Robert and Juste 1997). The application of these fertilizers can therefore lead to an unavoidable enrichment of cadmium soils. This is also the case for chromium, zinc, nickel, manganese, or cobalt, which, as impurities in fertilizers, are a significant supply source of soil. Equally, the use of traditional organic soil improvers, such as farmyard manure or slurry, will contribute to the increase in content of the heavy metal of the soil.

4.2 Pesticides

Traditionally, the main purposes of the use of chemicals are the enrichment of soil by various nutrient supply (fertilizers) or crop protection against insects and animals (pesticides). Pesticides are substances (chemical compounds and naturally occurring phytochemicals) that are used to kill pests in agricultural as well as household practices (Damalas and Eleftherohorinos 2011). They include compounds labeled as insecticides (organochlorines, organophosphates, carbamates, and pyrethroids), rodenticides (arsenic trioxide, barium carbonate, and anticoagulants), herbicides (paraquat, diquat, and 2, 4-dichlorophenoxyacetic acid), fungicides (dithiocarbamates and captan), and fumigants (ethylene dibromide and methyl bromide).

Recently, metals have found applications in designer chemicals, like agricultural and antimicrobial pesticides. The vast majority of the registered pesticides are organic and are made as fungicide or algaecide or insecticide or rodenticide. A study conducted on glyphosate toxicity of formulants and heavy metals in glyphosate-based herbicides and other pesticides showed that the sum of heavy metals in formulations after their different recommended dilutions can reach up to 80 ppb. It becomes obvious that the diluted GBH formulations are the most contaminated in general and pose a higher risk of contamination of soils and edible plants, especially in the case of As. Of 11 glyphosate-based herbicides, 6 exceeded the permitted levels in water even after recommended dilutions (1.5–15%) for agricultural or garden uses (Defarge et al. 2018).

5 Exposure Through Water

Supply of safe drinking water is crucial to human life, and safe drinking water should not impose a significant risk to humans (WHO 2011). Drinking water is mainly produced from surface water, groundwater, and desalinating seawater, with desalination satisfying a significant fraction of the drinking water demand in water-scarce regions (Kim et al., 2015). The sources of drinking water are likely to be polluted by heavy metals (Bryan and Langston 1992). Trace metals may be present in aquatic ecosystems as a result of natural processes, especially volcanic eruptions, weathering soils and rocks, as well as from human activities.

The factors affecting the release of trace metals from primary materials and soil and their solution and stability in water are solubility, pH, adsorption characteristics, hydration, coprecipitation colloidal dispersion, and the formation of complexes. As many plants are known to selectively concentrate various metal elements, the concentration of trace metals in the water will be affected and may become available during the decomposition of these plants. Moreover, the corrosion of the distribution system may also increase the concentration of trace metals in water before it reaches the consumer. Lead, copper, zinc, aluminum, and bronze are the elements most frequently encountered at the level of tap water at the consumer level (CSDW 1977).

6 Exposure Through Food

As stated above, there are several routes through which humans can be exposed to heavy metals, including ingestion of contaminated food. Both plants and animals can bioaccumulate heavy metals from the environment within their tissues. Since these plants and animals can be used as sources of food, these heavy metals imply a high risk to human health by expanding many diseases, and that is the reason why most of the major world governments and organizations have studied the effects of heavy metals, primarily lead, cadmium, mercury, and arsenic, on human health. European legislation lays down maximum allowed limits in foodstuffs. EU regulations cover the following heavy metals: mercury, lead, and cadmium.

Mercury comes in elemental, inorganic, and organic forms. Inorganic mercury is converted to organic forms in nature. It is considered to be one of the most toxic metal elements found mainly in fish and fishery products. Methylmercury is the main form in which mercury is present at over 90% than other forms of mercury in fish and other marine animals and in higher amounts in long-lived predator fish. It is easily absorbed into the intestinal system and readily enters the brain, especially the brain of a developing fetus.

Lead is the most commonly used metal. It has entered many agricultural products as chemical fertilizer, herbicide, sewage treatment, and contamination of soil by sewage. This metal is significantly toxic and accumulates in the body, which results in acute poisoning in humans (Tajkarimi et al. 2008). Lead is present at low concentrations in most foods. Offal and mollusks may contain higher levels. Contamination of food during processing or food production in contaminated areas is the main reason for enhanced lead intake viafoodstuffs. The hematopoietic system, nervous system, and renal system are the three main body systems sensitive to this metal (Naseri et al. 2015; Zahir et al. 2005).

Cadmium is an element that can contaminate groundwater supplies, which inevitably affects crops and different animal (Binns et al. 2003). Most foods such as cereals, fruit, vegetables, meat, and fish often have low levels of cadmium. The highest levels of cadmium are found in the offal (kidney and liver) of mammals and in mussels, oysters, and scallops. Certain wild mushrooms may also contain high levels, as can rice grown in certain geological areas where the soil is rich in cadmium. The International Agency for Research on Cancer (IARC) has classified cadmium and cadmium compounds as carcinogenic to humans (Group 1), meaning that there is sufficient evidence for their carcinogenicity in humans (IARC 1993, 2009).

6.1 Food Dietary Intake of Some Heavy Metals and International Recommendations

It is well recognized that some metals such as iron (Fe), zinc (Zn), and copper (Cu) are essential to human health. They are recognized by their role as metalloenzymes and as a cofactor of a large number of enzymes (FDA 2001). Beyond specific concentrations, toxic effects are observed (Singh and Garg 2006). Olalla et al. (2004) have determined that the adequate range for the proper functioning of the body is between 1.5 and 3 mg/day for copper and between 12 and 15 mg/day for zinc. The presence of some heavy metals, like mercury, lead, and cadmium, in the human body even at lower concentration is toxic and draws scientific concern as these are considered responsible for affecting health.

6.1.1 Mercury

The contribution of fish to the total intake of mercury varies from a low of 20% in Belgium and the Netherlands, to a high of 85% in Finland and the United States, with France and the United Kingdom in between (35%) (Galal-Gorchev 1993). In contaminated freshwater areas, mercury levels of 500–700 μg/kg are often found in fish, and in large carnivorous saltwater species such as shark and tuna, it normally falls in the range of 200–1500 μg/kg. Levels in fish from unpolluted waters are found to vary, but not exceeding about 200 μg/kg, and levels in mollusks and crustacea are rarely above 100 μg/kg. For grains, cereal products, vegetables, fruit, and meat, several studies have shown that mercury levels are generally below 30 μg/kg (UNEP 1992).

For mercury, a provisional tolerable weekly intake of 300 μg per person (equivalent to 5 μg/kg of body weight) has been established, of which no more than 200 μg (3.3 μ/kg) should be methylmercury for the general population, but it is important to note that pregnant women and nursing mothers are likely to be at greater risk from the adverse effects of methylmercury. The available data were considered insufficient to recommend a specific methylmercury intake for this population group (UNEP 1992; WHO 1989).

6.1.2 Lead

The average dietary intake data of lead by adults between 1980 and 1988 in 25 countries ranged from 1 to 63 μg/kg bw/week. In this period, the intakes slightly exceeding or approaching the provisional tolerable weekly intake (PTWI), which is of the order of 50 μg/kg bw/week, were reported for the average adult in Cuba, India, Italy, and Thailand. The lowest intake was reported by the United States. Furthermore, the lead intake for "extreme" adult consumers in Australia was about 17 μg/kg bw/wk. (approximately four times the intake of the "average" adult). Similarly, a mean intake of 25 μg/kg bw/wk. was reported in New Zealand. In Denmark and the United Kingdom, the average adult weekly intake was 8 μg/kg bw and 7 μg/kg bw/wk., respectively. In the monitoring program, emphasis was placed on staple foods such as cereals and potatoes and on foods that are most likely to contain high levels of lead (canned food, shellfish) (Galal-Gorchev 1993).

The Joint FAO/WHO Expert Committee on Food Additives (JECFA) established a provisional tolerable weekly intake (PTWI) for lead of 50 μg/kg of body weight to adults (WHO 1978). A guideline value of 0.05 mg/liter has been recommended for lead in drinking water (WHO 1984).

6.1.3 Cadmium

The national regulatory limits for cadmium from all sources from 31 countries vary from 10 μg/kg in milk or eggs to 2000 μg/kg in fish and shellfish, and the established PTWI is 7 μg/kg body weight. With the exception of Thailand, all reported intakes are below the PTWI of 7 μg/kg bw (UNEP 1992).

Cereals and their products, followed by potatoes and other vegetables, are ranked as the largest contributors to intake of cadmium in Canada, Denmark, Finland, the Netherlands, and the United States. The little intake contribution of this metal element is provided by fruit, meat, poultry, and dairy products (Galal-Gorchev 1993).

The JECFA has established a PTWI of cadmium of 7 μg/kg bw, applicable to adults as well as infants and children. A guideline value of 0.005 mg/liter has been recommended for cadmium in drinking water (WHO 1984).

6.2 Hazard Characterization and Risk Assessment

The data in this part are based on the French Total Diet Study conducted by the French National Institute for Agricultural Research (INRA) between 2000 and 2004 on 338 food items (Leblanc et al. 2005).

6.2.1 Mercury

Current epidemiological data strongly suggest that methylmercury is a neurotoxic substance responsible for delayed psychomotor development in children. With a view to providing an additional precaution regarding the potential impact of methylmercury on the neurological development of the fetus, the JECFA reevaluated the provisional tolerable weekly intake (PTWI) in 2003, lowering it to 1.6 μg/kg body weight (WHO 2003).

In terms of risk assessment, 38% of the samples analyzed showed mercury levels above the limit of detection (LOD) of 6 mg/kg of fresh weight.

The food groups that have shown significant mercury levels are the fish group and the chocolate group with mean values of 62 μg/kg and 42 μg/kg mg, respectively. The other food groups contain less than 17 μg/kg.

6.2.2 Lead

Lead is a cumulative toxicant that affects multiple body systems. It is particularly harmful to the system hematopoietic, nervous system, kidneys, and male reproductive system. In addition, several studies have shown that the major toxic effect of lead during the development of fetus can cause lasting neurobehavioral deficit in childhood. In 2000, the JECFA confirmed the provisional tolerable weekly intake of 25 μg/kg body weight (WHO 2000).

According to the same study, 75% of the samples analyzed show levels of lead above the limit of detection (LOD) of 5 μg/kg of fresh weight. Lead is found present at an average level between 0.05 and 0.1 mg/kg for the organ meats group and shellfish, and the other groups mainly present levels less than 0.04 mg/kg.

6.2.3 Cadmium

The International Agency for Research on Cancer (IARC) has classified cadmium and cadmium compounds as carcinogenic to humans (Group 1), meaning that there is sufficient evidence for their carcinogenicity in humans (IARC 1993, 2009).

The cadmium accumulates primarily in the kidneys, and its biological half-life in humans is between 10 and 30 years (WHO 2008). This accumulation may lead to irreversible renal tubular dysfunction, which results in increased excretion of low molecular weight proteins in the urine. The provisional tolerable weekly intake is confirmed by the JECFA in 2003 at the level of 7 μg/kg body weight (WHO 2003).

Still referring to the same study, 31% of the food samples display cadmium levels < LOD of μg/kg of fresh weight. Cadmium is found at an average level between 0.05 and 0.1 mg/kg in offals and shellfish; the majority of other food groups contain less than 0.02 mg/kg.

7 Conclusion

Because of the large production and immoderate consumption, the worldwide practice has exposed consumers to carcinogenic and pathogenic risks from contaminated foodstuffs. Heavy metals are considered toxic substances and persistent pollutants that are still found throughout the Earth's crust, posing risks to ecological and human health. In fact, exposure to heavy metals brings potential threats for major diseases such as neurotoxicity, infertility, risk of diabetes, immune suppression, risk of cardiovascular disorders, renal damage, birth defects, and cancer. The sources of heavy metals in food crops necessitate specific attention to determine the actual metal toxicity. In different countries, the current situation analysis of trace metal contaminations leads to conclude that there are hotspots suffering from agrochemicals and domestic wastes such as fertilizers and pesticides.

As they are nondegradable, appropriate methods need to be established for their efficient removal from the environment. Furthermore, to ensure a complete understanding of disease pathology likewise molecular and cellular pathways involved in this regard, more risk assessment research and comparative concentrations to international standards set for humans and ecosystem health are required.

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