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# DIOXINS AND FURANS CONTAMINATION OF FOOD AND THEIR TOXICOLOGICAL IMPLICATIONS ON THE HUMAN BODY MINI-REVIEW

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***Abstract***

*Dioxins (sum of polychlorinated dibenzo-p-dioxins - PCDDs) and furans (polychlorinated dibenzofurans - PCDFs), are polychlorinated aromatic compounds with high toxic potential, which persist in the environment. Their degradation is extremely slow, they accumulate in the human body mainly through the consumption of contaminated food (in more than 90% of cases) and can not be destroyed by cooking or metabolized by living organisms. This study aims to underline the importance of their determination through advanced analytical methods such high-resolution gas chromatography coupled with high resolution mass spectrometry (HRGC-HRMS), in order to increase the food safety.*

***Keywords:*** *dioxins, food, furans, HRGC-HRMS.*

## INTRODUCTION

Dioxins and furans are a group of chemical substances, with high toxic p otential, which persist in the environment and they accumulate in the living organisms through the food chain.
Dioxins as referred to in the Commission Regulation (EC) No 1881/2006, and replaced by 1259/2011, cover a group of 75 polychlorinated dibenzo-*p*-dioxin (PCDD) congeners and 135 polychlorinated dibenzofuran (PCDF) congeners, of which 17 are of toxicological concern. In order to be able to sum up the toxicity of these different congeners, the concept of toxic equivalency factors (TEFs) has been introduced to facilitate risk assessment and regulatory control. TEFs values were proposed first by the World Health Organisation (WHO), in 1997 in Stockholm, Sweeden. In 2005, they were updated by the same organisation (Van den Berg et al. 1998; Van den Berg et al. 2006) (Table 1).
To the compound with the highest toxicity, 2,3,7,8 - TCDD, was assigned the biggest TEF value, 1.

Dioxins (sum of polychlorinated dibenzo-*p*-dioxins (PCDDs)) and polychlorinated dibenzofurans (PCDFs) are expressed as World Health Organisation (WHO) toxic equivalent using the WHO-toxic equivalency factors (WHO-TEFs) in pg/g fat.

Table 1. TEFs proposed by WHO for PCDDs and PCDFs

| | **WHO-TEF$_{95}$** | **WHO-TEF$_{05}$** |
|---|---|---|
| **PCDDs** | | |
| 2,3,7,8-TCDD | 1 | 1 |
| 1,2,3,7,8-PeCDD | 1 | 1 |
| 1,2,3,4,7,8-HxCDD | 0.1 | 0.1 |
| 1,2,3,6,7,8-HxCDD | 0.1 | 0.1 |
| 1,2,3,7,8,9-HxCDD | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-HpCDD | 0.01 | 0.01 |
| OCDD | 0.0001 | *0.0003* |
| **PCDFs** | | |
| 2,3,7,8-TCDF | 0.1 | 0.1 |
| 1,2,3,7,8-PeCDF | 0.05 | *0.03* |
| 2,3,4,7,8-PeCDF | 0.5 | *0.3* |
| 1,2,3,4,7,8-HxCDF | 0.1 | 0.1 |
| 1,2,3,6,7,8-HxCDF | 0.1 | 0.1 |
| 1,2,3,7,8,9-HxCDF | 0.1 | 0.1 |
| 2,3,4,6,7,8-HxCDF | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-HpCDF | 0.01 | 0.01 |
| 1,2,3,4,7,8,9-HpCDF | 0.01 | 0.01 |
| OCDF | 0.0001 | *0.0003* |

## MATERIALS AND METHODS

For this paper, we consulted series scientific articles, between 1988 and 2012, including the European Commission Regulations, using as keywords, the terms: dioxins, furans, food.

## RESULTS AND DISCUSSIONS

### 1. FOOD CONTAMINATION

Dioxins and furans are secondary products resulted from: chemical reactions (carbo-chemical processes, wood treatment with penta chloro-phenol, paper whitening, herbicides production etc.), combustion processes (wood and wood waste, oil and coal combustions), incineration of municipal, hospital and industrial wastes, technological incineration of dangerous wastes, incineration of the plant wastes on the fields, big fires in which can be involved big quantities of materials containing chlor (for example, PVC), industrial accidents and occasional fires (Zedeck, 1998; Scialli, 2001; Schecter, 2001; McKay, 2002).

The decomposition of the dioxins and furans in the environment is extremely slow, reason why, dioxins can concentrate in the food chain, animals getting to have in their body (by bioaccumulation) much higher concentrations than plants, water or even soil. The accumulation of the dioxins in the human body, occurs mainly through the contaminated food consumption (in more than 90% of the cases). Air inhalation and absorbtion by the dermis, are considered to be minor contamination sources with dioxins and furans for the human body (Travis, 1991; Ganesh, 1995; Liem, 1999).

Dioxins and furans from foods can not be destroyed by preparation methods, can not be metabolized by the organism and can not be eliminated by faeces or urine, but contrary, they accumulate, their concentration getting higher and higher from one food to another, in body′s fat deposits.

According to the US Environmental Protection Agency, the highest dioxins and furans concentrations are found in beef (longer the animal lives, higher concentrations accumulates). Follows, milk and milk products (yogurt, cream, butter, cheese etc.), chicken meat, pork, fish and eggs. Likewise, the presence of these toxic compounds in human milk, continues to be a major risk for the breast feed babies health (Schuhmacher, 2004).

The contamination of food with dioxins and furans is a thorny problem all over the world. Unfortunately in Europe there were a lot of cases related to food products contamination. In Germany, in 1997, was detected a contamination with dioxins, of some milk, butter, beef and veal samples. The contamination source was found to be the dehydrated citrus pulp, imported from Brazil, and used in animals feed. The concentration in dioxins found in this pulp was from 20 to 100 times higher than the maximum level. After removing the contaminated citrus pulp from animals feed, the concentration of the dioxins in the milk, decreased substantially (Malisch, 2000).

Ramos et al. (1997) determined the dioxins and furans content, of some milk samples from different farms in Spain. The milk from neighboring areas with different sources of dioxins and furans contamination (waste incinerator, chemical plant, paper mill factory), presented significant concentrations of dioxins, unlike the milk taken from „control farms″ (located in rural areas, without any specific contamination sources), where the concentrations of dioxins, were below the maximum admissible limits.

Lovett et al. (1998), studied the contamination degree with dioxins and furans in eggs and poultry, from farms situated in different areas of Great Britain. Of course, the eggs and poultry from a farm situated close to a chemical waste incinerator, had very high dioxins and furans concentrations, far beyond the limits permitted by legislation. The scientists reported as well, the presence of dioxins and furans, in samples from farms located in rural areas, apparently unexposed to sources of dioxins and furans contamination.

Another very serious contamination with dioxins and furans, of poultry and derivated products, was registered in Belgium, in 1999. The contamination source was found to be a lot of recycled fat (containing a very high dioxins and furans concentration), used for obtaining feed for the chickens (Bernard, 1999). Since 1999, Belgium, has established a comprehensive program for monitoring the concentration of dioxins and furans in feed, poultry, beef and pork, using both screening

and confirmatory methods, high resolution gas-chromatography, coupled with high resolution mass spectrometry (HRGC-HRMS).

In 2000, Engwall and Hjelm reported a dioxins and furans contamination, for a batch of carrots cultivated on a land irrigated with sewage. They compared their results with a control batch, irrigated with non-contaminated water, where the presence of dioxins wasn′t detected.

Researchers from Spain and Finland (Schuhmacher, 2004), revealed through HRGC-HRMS analysis, that the breast milk from 15 mothers, living in the neighborhood of waste incinerators, had a significant higher content in dioxins and furans, expressed as a sum of dioxins (WHO-PCDD/Fs-TEQ), of 5.1 to 46.8 pg/g of fat.

In 2006, M. De Vries et al., presented the results of a study, undertaken in EU countries, that showed up that eggs obtained in organic farming system, have very high concentrations in dioxins and furans, between 0.4 and 19 pg/g fat, in many cases exceeding the maximum level, of 3 pg/g fat (Commission Regulation (EU) 1881/2006, replaced by 1259/2011).

In 2007, specialists from Hungary (Kasza et al.) reported the presence of dioxins in E-412 food additive (guar gum), imported from India, by a swiss company. German and French authorities, withdrawn from commercial the yogurts and cheeses which had in their composition guar gum from this lot.

In 2008, the Italian Ministry of Health in collaboration with the European Commission developed a comprehensive monitoring program for contamination with dioxins and furans of buffalo milk, in order to prevent the possible contamination of soft buffalo cheese. Using HRGC-HRMS, was confirmed that 25.8% of the total milk samples, weren′t consistent in terms of dioxins and furans content (Scortichini, 2009).

Marti-Cid et al., in 2008, studied the exposure degree to dioxins and furans contamination of Tarragona population (Catalonia, Spain), located near waste incinerators. In order to determine the dioxins and furans concentrations, were analyzed a series of foods (vegetables, cereals, fruits, fish, seafood, meat and meat products, eggs, milk and milk products, oils and fats), used frequently in the diet of this population. Using, HRGS-HRMS, it was found that the total intake of dioxins and furans to the overall population of the province of Tarragona was estimated to be 27.81 pg/g fat/ day. It has been revealed that animal products contribute at a rate of 78% to the dioxins and furans intake, in the diet of the population located in this area of Spain.

In 2008, was reported the contamination with dioxins and furans of pork meat, from some Irish farms. The contaminating source was found to be the feed used for feeding pigs (Tlustos, 2012).

In 2010, was detected the contamination with dioxins and furans of pork, poultry and eggs, from many German farms. The contamination source, as in most of the cases presented before, was the feed used for feeding animals, which contained oils with high dioxins and furans concentrations (Schwind, 2010).

## 2. TOXICOLOGICAL IMPLICATIONS

Dioxins and furans have many harmful effects on the human body, including immunotoxicity, hepatotoxicity, birth defects, endocrine disruption or induction of numerous enzymes. It is thought that dioxins and furans exert their effects by binding to a specific cellular protein known as the aryl hydrocarbon receptor (AhR) (Aoki, 2001), an intracellular ligand involved in the regulation of a very large number of genes (Mitrou et al., 2001).

In humans and other vertebrates, the toxic responses to dioxins and furans may include: nervous system pathology, dermal toxicity such as skin cancer or dermal lesions, including rarely, chloracne or acne (the most known case in the world, the food poisoning of the Ukrainian presidential candidate, Viktor Yushchenko, in 2004), immune deficiency by affecting the hormones involved in the immune response of the body, immunosuppression induced by direct action on T and B lymphocytes, endocrine disruptions, including diabetes and thyroid disorders, decreased pulmonary functions, carcinogenity-hepatic, genital or pulmonary cancer (especially caused by 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), which was evaluated as group 1 carcinogenic to humans by International Agency for Reasearch on Cancer, in 1997), reproductive and developmental toxicity by causing spontaneous abortions, infertility and

disorders of endocrine glands, teratogenic effects such as heart defects, hydrocephalus, spina bifida (WHO, 1997; CDC, 1998; Otles, 2003; EFSA, 2012).

## 3. FOODS CONTRIBUTING TO THE DIETARY EXPOSURE

According to the 2012′s EFSA Report, seven main groups of food should be taken into account when it comes to infants, children, adolescents, adults, elderly and very elderly population groups, dietary exposure: fish and seafood products, milk and dairy products, meat and meat products, eggs and eggs products, oils and fats from animal and plant origin, foods for infants and young children and other foods, such as dietary supplements and honey.

According to the same report, in almost all adolescents, adults, elderly and very elderly populations, fish and seafood products are the main contributor to the total dietary exposure, 30.2-75%, followed by meat and meat products 8.8-34.4% or milk and dairy products 7.3-24.6%. In infant and children cases, the major contributor was milk and dairy products with 27.5-49.6%, followed by fish and seafood products 10.7-35.8% or meat and meat products 10.4-33.7%.

In Table 2, are presented the maximum levels for the dioxins and dioxin-like polychlorinated biphenyls (PCBs) content in foodstuffs:

Table 2. Maximum levels for dioxins and furans in foodstuffs (CR (EU) 1259/2011)

| **Foodstuffs** | **Sum of dioxins (WHO-PCDD/F-TEQ)** | **Sum of dioxins and dioxin-like PCBs (WHO-PCDD/F-PCBs-TEQ)** |
|---|---|---|
| (*) Meat and meat products (excluding edible offal) of the following animals:<br>bovine animals and sheep<br>poultry<br>pigs | <br>2.5 pg/g fat<br>1.75 pg/g fat<br>1.0 pg/g fat | <br>4.0 pg/g fat<br>3.0 pg/g fat<br>1.25 pg/g fat |
| Liver of terrestrial animals referred to in (*), and derived products thereof | 4.5 pg/g fat | 10.0 pg/g fat |
| Muscle meat of fish and fishery products and products thereof, with the exemption of:<br>wild caught eel<br>wild caught fresh water fish, with the exception of diadromous fish species caught in fresh water<br>fish liver and derived products<br>marine oils<br>The maximum level for crustaceans applies to muscle meat from appendages and abdomen. In case of crabs and crab-like crustaceans (*Brachyura* and *Anomura*) it applies to muscle meat from appendages. | 3.5 pg/g wet weight | 6.5 pg/g wet weight |
| Muscle meat of wild caught fresh water fish, with the exception of diadromous fish species caught in fresh water, and products thereof | 3.5 pg/g wet weight | 6.5 pg/g wet weight |
| Muscle meat of wild caught eel (*Anguilla anguilla*) and products thereof | 3.5 pg/g wet weight | 10.0 pg/g wet weight |
| Fish liver and derived products thereof with the exception of marine oils referred to (***) | - | 20.0 pg/g wet weight |
| (***) Marine oils (fish body oil, fish liver oil and oils of other marine organisms intended for human consumption) | 1.75 pg/g fat | 6.0 pg/g fat |
| Raw milk and dairy products, including butter fat | 2.5 pg/g fat | 5.5 pg/g fat |
| Hen eggs and egg products | 2.5 pg/g fat | 5.0 pg/g fat |
| Fat of the following animals:<br>bovine animals and sheep<br>poultry<br>pigs | <br>2.5 pg/g fat<br>1.75 pg/g fat<br>1.0 pg/g fat | <br>4.0 pg/g fat<br>3.0 pg/g fat<br>1.25 pg/g fat |
| Mixed animal fats | 1.5 pg/g fat | 2.5 pg/g fat |
| Vegetable oils and fats | 0.75 pg/g fat | 1.25 pg/g fat |
| Foods for infants and young children | 0.1 pg/g wet weight | 0.2 pg/g wet weight |

## CONCLUSIONS

Dioxins and furans are widespread environmentally and biologically highly toxic stable polluants, all over the world, that accumulate in the living organisms. Human exposure to these chemicals is chronic and can provoke serious health effects and diseases, such as cancers or damages for the immune system. The major sources for dioxins and furans entering in the atmosphere are incineration and combustion processes. A major pathway of exposure for humans is through the consumption of fish and seafood products as main source, followed by meat and meat products and milk and dairy products. By reducing the environmental contamination with dioxins and furans, can be diminished the bioaccumulation in the food chain and this way reduced the intake levels and of course their toxic effects.

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