Dioxins in food chain

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Review

Summary

Dioxins and dioxin-like compounds include 29 different congeners of dioxins, furans and polychlorinated biphenyls (PCB). Toxicity of the listed compounds is very similar. The most toxic congener is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Toxic potential of other dioxins (PCDD) and furans (PCDF) is defined in relation to TCDD. Human exposure to dioxins mainly refers to exposure through food. When dioxins enter the organism, they are partly metabolized and eliminated from the organism, and partly accumulated in the fatty tissue. It has been legally regulated that the share of dioxins in food and animal food is expressed by the toxic equivalent (TEQ).

Key words: *dioxins, polychlorinated biphenyls, food*

Introduction

Dioxins represent a group of polychlorinated aromatic compounds of similar structure and similar physical and chemical properties. Out of 210 theoretically possible congeners, 75 of them belong to the group of polychlorinated dibenzo-p-dioxins (PCDD), whereas 135 congeners belong to the group of polychlorinated dibenzofurans (PCDF). Figure 1 shows general structures of PCCD and PCDF. Dioxins are wide- spread contaminants with no specific usage and they are not produced. They mostly appear as unwanted byproducts of different industrial processes, combustion in waste incineration, and in the production of certain chemicals (e.g. organochlorine pesticides and herbicides). Forest fires and volcanic eruptions are also a source of dioxins. Waste incineration is considered to be the highest causative agent of environmental contamination. Dioxins have hydrophobic character, and they are well soluble in fats. Since they are not water- soluble, they bind to sediment and organic matter in the environment. Dioxins are very stabile and resistant to chemical and microbiological degradation which makes them very stabile in the environment (Anon., 2010).

Toxicity of certain compounds of dibenzodioxins, dibenzofurans and PCBs differs significantly. Out of 210 theoretically possible congeners of dioxins and furans, expressedly toxic are only those where aromatic rings are substituted on 2-,3-,7- and 8- positions. The most toxic dioxin congener is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) (Marinković et al., 2010).

Polychlorinated biphenyls (PCB) are often mentioned along with the dioxins. PCBs are aromatic hydrocarbons where one or all ten hydrogen atoms from biphenyl molecules are replaced with a chlorine atom. Figure 2 shows a chemical structure of PCB. The usage of PCB in the past was widespread. The reason for that is their physical and chemical property of incombustibility, chemical stability, high boiling points and high dielectric constant. Production and usage of PCB have been banned in most countries, but in spite of that, large quantities of PCB have remained in different electronic equipment, plastic products and in buildings, i.e. in the used building material. There are 209 theoretically possible PCB congeners which can be classified to different groups according to their biochemical and toxic properties (Anon., 2001). Polychlorinated biphenyls, which are not substituted in the ortho- position and which are mono substituted in the ortho- position, show toxicological properties similar to dioxins. Because of that, such PCBs are often

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referred to as dioxin- like PCBs.

Regarding PCB, out of 209 congeners, the toxicity of 12 congeners is similar to toxicity of dioxins. Dioxins are significantly more toxic than PCB, whereas PCB quantities in the environment are several times higher than dioxin quantities. Therefore PCBs are found more often in food and animal feed.

Exposure to dioxins

Exposure to dioxins can also occur through inhalation, drinking water and skin absorption. A short time exposure to large quantities of dioxins can cause skin lesions such as cloracne, dark spots on the skin and it can cause changes in the function of liver. A long time exposure is connected to the weakening of the immune system, damaging of the nervous and endocrine system, and reproductive function. It is considered that of about 95% of human exposure to dioxins occurs through food of animal origin, where meat, dairy products, eggs and fish are the main source of dioxins (Anon., 2010a). When dioxins enter the human body, one part is metabolized and excreted, and the other part is accumulated in the fatty tissue. In order for dioxins to be eliminated from the body, they have to convert to polar derivatives. The process of excretion from the body depends on the absorbed quantity, age and quantity of fatty tissue (Marinković et al., 2010). Researches of TCDD excretion from the body showed certain differences within human population. According to those researches, TCDD is excreted more quickly from the bodies of males and younger people, whereas slower excretion is noticed at females and older people (Aylward et al., 2005).

Dioxins belong to the most toxic organic compounds. Researches made on animals showed that chronic exposure to dioxins can cause several types of cancer. Based on those studies and available epidemiologic data, World Health Organization (WHO), i.e. International Agency for Research on Cancer (IRAC) classified 2,3,7,8-TCDD to compounds which are cancerous for people (group 1). Still, it should be mentioned that 2,3,7,8-TCDD doesn't affect directly the genetic material and that there is a level of exposure below which the risk of cancer is negligible (Anon., 2010).

Dioxins are usually found as complex compounds of PCDD, PCDF and PCB congeners. Therefore the concept of Toxicity Equivalency Factor (TEF) was developed in the aim of risk assessment, in order to estimate the cumulative toxicity of the compounds of dioxins and dioxin-like PCBs. The most toxic congener 2,3,7,8-TCDD was taken as reference congener, and its TEF value is 1. Relative toxicity of all other dioxins (PCDD, PCDF and PCB) is shown in relation to the reference congener. Toxic effect of dioxin compound is the sum of TEF values of individual compounds multiplied by their concentration. The obtained value is called Toxic equivalency (TEQ) (Anon., 2001b).

$$TEQ = \sum_{i=1}^{n} |c_i \cdot TEF_i|$$

Where:

TEQ- Toxic equivalency

c_i- concentration of individual congener

TEF- Toxicity Equivalency Factor

Figure 1. Chemical structures of PCDD and PCDF

Table 1. **Values of Toxicity Equivalency Factor determined in 1998 (TEF_{WHO98}) and during the last re-evaluation in 2005 (TEF_{WHO05}) (EFSA, 2010).**

Chemical compound	TEF_{WHO98}	TEF_{WHO05}	Chemical compound	TEF_{WHO98}	TEF_{WHO05}
Chlorinated dibenzo-p-dioxins			Unsubstituted PCB at the ortho position		
2,3,7,8-TCDD	1	1	PCB-77	0.0001	0.0001
1,2,3,7,8-PeCDD	1	1	PCB-81	0.0001	0.0003
1,2,3,4,7,8-HxCDD	0.1	0.1	PCB-126	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1	PCB-169	0.01	0.03
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			
Chlorinated dibenzofurans			Mono-ortho substituted PCB		
2,3,7,8-TCDF	0.1	0.1	PCB-105	0.0001	0.00003
1,2,3,7,8-PeCDF	0.05	0.03	PCB-114	0.0005	0.00003
2,3,4,7,8-PeCDF	0.5	0.3	PCB-118	0.0001	0.00003
1,2,3,4,7,8-HxCDF	0.1	0.1	PCB-123	0.0001	0.00003
1,2,3,6,7,8-HxCDF	0.1	0.1	PCB-156	0.0005	0.00003
1,2,3,7,8,9-HxCDF	0.1	0.1	PCB-157	0.0005	0.00003
2,3,4,6,7,8-HxCDF	0.1	0.1	PCB-167	0.00001	0.00003
1,2,3,4,6,7,8-HpCDF	0.01	0.01	PCB-189	0.0001	0.00003
1,2,3,4,7,8,9-HpCDF	0.01	0.01			
OCDF	0.0001	0.0003			

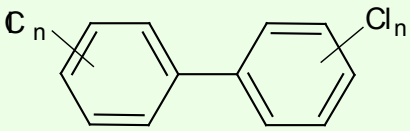

Figure 1. Chemical structures of PCDD and PCDF

Through the International Program on Chemical Safety (IPAC), WHO has been implementing and re-evaluating TEF values for dioxins and dioxin- like compounds for the last two decades. The last re-evaluation was conducted in 2005 when TEF values for octa- chlorinated dioxins and furans and polychlorinated biphenyls were changed. Table 1 shows TEF values determined at the last re-evaluation by WHO in 2005. Since there was a change in TEF value for some compounds, the TEF values determined in 1998 were also shown for better understanding (Anon., 2010).

Presence of dioxins in food

A strict quality control system and a systematic food monitoring are not a sufficient guarantee of food safety. It has also been proved by the recent incident related to the presence of dioxins in food and animal feed that happened in Germany. Animal feed was contaminated by dioxins while adding fatty acids intended for technical use. It was determined that fatty acids were contaminated by dioxins which originated from the production of biodiesel. It is assumed that this incident included about 4800 farms in Germany. So far there is no information that contaminated fatty acids were delivered outside Germany (Anon., 2011).

Incidents related to discoveries of dioxins in food are often a consequence of contamination of animal feed. At the end of 2008 in Ireland, there was discovered a 200 times larger dioxin quantity than permitted. Because of that, a large quantity of pork and pork products were withdrawn from the market, which was the largest withdrawal of food from the market caused by a chemical contamination so far. In this case as well, the main source of dioxin contamination was animal feed. In July 2007, there were found large dioxin concentrations in food additive "guar gum" which is used in small quantities as thickener in meat and dairy products, desserts and delicacies. The source of contamination is the above mentioned thickener originating from India which also contained large quantities of the forbidden pesticide pentachlorophenol. Pentachlorophenol was contaminated by dioxins which probably appeared during its production. In the years of 2004 and 2006 there were recorded two incidents in the Netherlands related to the increased dioxin quantities. In one case there was an increased quantity of dioxins in milk, and the cause of contamination was animal feed, i.e. clay which was used in the production of animal feed. The other incident with dioxins was related to the contamination of animal feed, and the sources of dioxins were fats which were added to animal feed. In Belgium in 1999 there were found large concentrations of dioxins in chicken and eggs, and in Germany in 1998 dioxin was found in milk. In both cases the source of contamination was animal feed (Anon., 2010a).

Legislation

The concern of the public, scientific and supervisory institutions related to the long- term exposure to small quantities of dioxins and their influence on human health has increased significantly after the dioxin crisis in Belgium in 1999. European Commission – Scientific Committee on Food (EC SCF) estimated in 2000 and 2001 that there is a public health risk of dioxins and dioxin- like PCBs from food (Anon., 2000; Anon 2001). European Commission – Scientific Committee on Animal Nutrition (EC SCAN) has adopted the opinion on contamination of animal feed by dioxins and contribution to contamination of animal feed, contamination of food of animal origin (Anon., 2000a). The listed opinions of scientific committees represented the basis for making boundaries related to the presence of dioxins and dioxin- like PCBs in food and animal feed, and they initiated the making and acceptance of many legal acts related to the presence of dioxins and dioxin- like PCBs in food. The legal acts of the EU related to dioxins in food and animal feed are:

- Commission Regulation (EC) No 1881/2006/EC – determines the highest shares of certain contaminants
- Commission Regulation (EC) No 1883/2006/EC – proscribes the methods of sampling and analysis in the aim of official control of levels of dioxins and dioxin- like PCBs in food
- Commission Regulation (EC) No 152/2009/EC – proscribes the methods of sampling and analysis in the aim of official control of levels of dioxins and dioxin- like PCBs in animal feed
- Commission Directive 2002/32/EC – determines the highest shares of unwanted compounds in animal feed
- Commission Directive 2002/70/EC i 2005/7/EC – determines conditions for determining levels of dioxins and dioxin- like PCBs in animal feed
- Commission Recommendation 2006/88/EC – relates to decreasing of the presence of dioxins, furans and PCBs in food and animal feed
- Commission Recommendation 2006/794/EC – relates to the monitoring of levels of dioxins, dioxin- like PCbs and other PCBs in food
- Commission Recommendation 2004/704/EC – relates to the monitoring of levels of dioxins,

dioxin- like PCBs and other PCBs in animal feed

The presence of dioxins and dioxin- like PCBs in food and animal feed in the Republic of Croatia was regulated by the following Ordinances:

- Ordinance on maximum levels for certain contaminants in foodstuffs (Official gazette No. 154/08). This ordinance has adopted the regulations 1881/2006/EC
- Ordinance laying down the methods of sampling and the analysis for the official control of the levels of dioxins and dioxin-like polychlorinated biphenyls in foodstuffs (Official gazette No. 45/2008). This ordinance has adopted the regulations 1883/2006/EC.
- Ordinance on undesirable substances in animal feed (Official gazette No. 80/2010 and Official gazette No. 111/2010). This ordinance has adopted the regulations 2002/32/EC.
- Ordinance laying down the methods of sampling and the analysis for the official control of animal feed (Official gazette No. 146/2010). This ordinance has adopted the regulations 2009/152/EC

Conclusion

For the last couple of years there were several incidents which have pointed to a problem of contamination of food by dioxins. After the incident in Belgium in 1999 there was brought a series of legal regulations that regulate the presence of dioxins in food and animal feed. Recommendations were also brought for decrease of their presence in the environment. The recent occurrences in Germany have shown that regardless of all the measures taken, contamination of food by dioxins still remains a burning issue.

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