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Pentachlorophenol from an old henhouse as a dioxin source in eggs and related human exposure

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High levels of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were detected in free-range eggs, and these levels reached a concentration of 29.84 ± 7.45 pg of WHO-TEQ/g of fat. This value exceeded the EU maximum permitted level of 2.5 pg of WHO-TEQ/g of fat for PCDD/F congeners by twelve-fold. A chemical analysis (HRGC-HRMS) revealed elevated amounts of OCDD, OCDF, HxCDD, HpCDD and HpCDF. During the investigation, samples of feed, soil, wall scrapings, wooden ceiling of the henhouse and tissues from laying hens were examined for dioxin contents (30 samples altogether). The long and complicated investigation found that the source of dioxins in the poultry farm was pentachlorophenol-treated wood, which was used as structural components in the 40-year-old farm building adapted to a henhouse. The wooden building material contained PCDD/Fs at a concentration of 3922.60 ± 560.93 pg of WHO-TEQ/g and 11.0 ± 2.8 μg/kg of PCP. The potential risk associated with dioxin intake was characterized by comparing the theoretically calculated weekly and monthly intakes with the toxicological reference values (TRVs), namely the Tolerable Weekly Intake (TWI) and Provisional Tolerable Monthly Intake (PTMI) values of 14 pg of WHO-TEQ/kg of bw and 70 pg of WHO-TEQ/kg of bw, respectively. The intake of dioxins estimated for high egg consumers (approximately 5–6 eggs/week) exceeded the TWI and PTMI values, which may pose a risk of delayed adverse health effects. The estimated dose of PCDD/Fs and DL-PCBs for children consuming 5 eggs per week exceeded the TWI by as much as 450% because of their nearly 5-fold-lower body weight. Although the dioxin intake estimated for the average consumption of eggs in the general population did not exceed any of the TRVs applied (58.7% TWI and 51.1% PTMI), such a situation should be considered unacceptable from a public health perspective because eggs are not the only source of these contaminants.

1. Introduction

Food contaminated with chemical compounds plays an important role in our health. Persistent and bioaccumulative substances, for which food is the main route of human exposure, require special attention. The presence of persistent chemical impurities in the surrounding environment requires constant action to protect people from the consumption of food contaminated with dioxins.

In everyday language and in science, the term “dioxins” covers a large group of toxic organic chemicals, comprising 75 toxic polychlorinated dibenzo-*p*-dioxins (PCDDs) and 135 polychlorinated dibenzofurans (PCDFs). Due to their common mechanism of action, twelve dioxin-like polychlorinated biphenyls (DL-PCB) congeners are also included in this group (Denison et al., 2011, Schecter et al., 2006). Dioxins and dioxin-like compounds have been found in air, soil, sediments, vegetation, animals, and human tissues all over the world (Piskorska-Pliszczynska and Maszewski, 2014). Widespread dioxin and dioxin-like compounds have been classified as a high-potential toxicological hazard due to their bioaccumulation in the food chain, the danger of exceeding the maximum permitted levels for people and their toxicological profile (Domingo, 2014; Donato and Zani, 2010; European Food Safety Authority, 2012; Piskorska-Pliszczynska et al., 2014). Prolonged exposure, even at very low doses, may increase the risk of adverse health effects, such as endocrine imbalance, immune disorders, reproductive disturbances, cancer and neurobehavioral effects. The health effects of

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exposure to dioxins may manifest after many years, as well as in subsequent generations (Baccarelli et al., 2008; Mocarelli et al., 2008; Vested et al., 2014). Although human exposure to PCDD/Fs and PCBs can occur by various routes, food of animal origin is the main pathway with roughly 80–90% of the total exposure via fish, meat, dairy products and as much as 5–10% via poultry products (Focant et al., 2002).

Animal feed is considered the main cause of contamination of food of animal origin (Malisch and Kotz, 2014). Therefore, the European Community (EC) introduced the maximum permitted levels for feed and feed materials to protect food from excessive accumulation of dioxins (Directives: 2002/32/EC, 2002/70/EC, 277/2012/EU). However, the current permitted levels established for feed do not guarantee that food produced from animals will contain dioxin concentrations below the acceptable limits. Dioxin presence in tissues of food-producing animals may be associated with the contamination of commercial or non-commercial animal feed, poor feed-production practices, local pollution, and environmental sources (Hsu et al., 2010; Kudryavtseva et al., 2013; Schwarz et al., 2014). In recent years, a number of research papers have indicated that the soil is a source of contamination. Soil is a natural reservoir for dioxins and other persistent organic pollutants (Diletti et al., 2005; Fernandes et al., 2011; Hoang et al., 2014; Lin et al., 2012; Piskorska-Pliszczynska et al., 2014). The amount of dioxins and PCBs released into the surrounding environment from uncontrolled sources, such as domestic hearths (wood- and coal-burning stoves and fireplaces) and the burning of organic and synthetic materials in courtyards and gardens, has increased (Estrellan and Fukuya, 2010; Solorzano-Ochoa et al., 2012; Wyrzykowska et al., 2009). It has been estimated that uncontrolled sources account for over 50% of the contamination in Poland [www.kibize.pl].

Wood treated with preservatives used in animal housing, farm equipment and bedding materials may also be a dioxin source (Brambilla et al., 2009; Fries et al., 2002; Hansen et al., 1989). Food-producing animals may also be exposed to pentachlorophenol (PCP) from the treated wood elements of farming facilities. PCP is a toxic substance of great environmental concern. For many years, it was widely used as a bactericide, fungicide, herbicide, defoliant, and wood preservative (Gebefugi et al., 1979; Huwe et al., 2004). The main contaminants of this synthetic substance were PCDDs and PCDFs. PCP-treated wood was used extensively in animal housing and confinement facilities until the 1980s, when its use was limited and restricted. It was found in all environmental elements (air, soil, and water) as a result of its past widespread usage. PCP is released directly into the atmosphere via volatilization from treated wood surfaces, has been associated with elevated levels of dioxins in livestock and is also the cause of egg contamination (Brambilla et al., 2009; Diletti et al., 2005; Fochi et al., 2006; Ryan et al., 1985). One of the last well-known incidents was the contamination of guar gum from India. Guar gum is commonly used vegetable origin food additive (E412). In July 2007, the EU issued a health warning to the member states after high levels of dioxins were detected in guar gum used as a food additive. The source was traced to Indian guar gum contaminated with PCP (Decision 2008/352/EC; Reg. 258/2010/EU; Wahl et al., 2008). At present, food contamination with dioxins caused by PCP is quite rare due to the limited use of PCP.

As it turns out, PCP-treated building timber used in farm buildings still constitutes a threat as a source of dioxins. Within the framework of national food surveys, particular attention was paid to hen eggs in connection with the recommendations of the European Commission 711/2013/EU. During routine testing, very high levels of PCDDs and PCDFs were detected in a free-range egg sample. The PCDD/F concentration exceeded the EU maximum permitted level of 2.5 pg of WHO-TEQ/g of fat for PCDD/F congeners (EU Regulation 1259/2011) by twelve-fold. In cases in which the allowable dioxin level in food is exceeded, investigation actions are taken to determine the contamination sources. The identification of PCDD and PCDF sources and a route of their entry in to the food chain at a farm level and the assessment of the potential health risks from the consumption of these eggs became the main tasks of our investigation.

2. Materials and methods

2.1. Sampling

In Europe, the labeling and hygiene requirements for producers of table eggs from laying hens are described in few EU documents (Council Directive 1999/74/EC; Council Directive 2001/4/EC; Reg. 1234/2007/EC; Reg. 589/2008/EC; Reg. 598/2008/EC). About 70 percent of eggs are produced in ways that are described as 'intensive', which is named battery cage production. The alternative to intensive poultry farming is free-range farming (allows chicken to roam freely), production in close barn (barn eggs) and organic system (similar to free-range, but with restriction on the routinely used feed, medication, food additives). The hen eggs has come from all four production methods as described in detail by EU law.

The hen egg samples were collected from farms throughout the country and a sample from each location contained 12 whole eggs. A total of 187 samples were analyzed. The type and number of eggs examined are shown in Table 1. From the poultry farm, where the content of dioxins in eggs was found at the unallowable level of 29.84 pg of WHO-TEQ/g of fat, the following samples were collected for laboratory analysis: feed, soil from the backyard, barn bedding materials, remains of building materials located in backyards or paddocks, scrapings from the walls of sheds, pieces of wood, waste, tissues from laying hens and nest eggs. All together thirty different samples from the contaminated chicken farm were collected by a Veterinary Inspection officer and sent to the NRL laboratory for testing.

2.2. Method of analysis

2.2.1. Chemicals and analytes

All of the organic solvents and chromatographic sorbents used were of purity suitable for the residue analysis. The PCDD/F and PCB standards were from the Cambridge Isotope Laboratory (Andover, MA, USA) and Wellington Laboratories Inc. (Ontario, Canada). A total of 35 PCDD/F and PCB congeners were the analytes of interest, including seventeen 2,3,7,8- substituted PCDD/F congeners, 12 congeners of DL-PCBs (PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189), and 6 non-dioxin-like polychlorinated biphenyls (NDL-PCBs) (PCB 28, 52, 101, 138, 153, and 180). The choice of analytes was in accordance with the relevant EU legislation for foodstuffs (Regulation 1259/2011/EU) and sampling and analytical methods for the official control of PCDD/Fs and PCBs (Regulations: 252/2012/EU, 589/2014/EU).

2.2.2. Extraction and clean-up procedure

After labeling with $^{13}C_{12}$ standards, all of the samples were extracted using accelerated solvent extraction. Hen eggs were extracted with methanol/toluene (70/30 v/v), whereas animal tissues and feed samples with dichloromethane/n-hexane (50/50 v/v). Soil, pieces of boards, scrapings from the walls, litter from a henhouse and pieces of the concrete floor were extracted with toluene. Purification was done with the use of multilayer silica, Carbopack C/Florisil and carbon columns. At first, extract were oxidized on a multilayer acid silica column and analytes were eluted with n-hexane. Dioxins and furans were eluted with toluene. PCBs were separated into two fractions on a Carbopack C/Florisil

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