Chemosphere 94 (2014) 13–19

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Polychlorinated dioxins, furans (PCDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs) and indicator PCBs (ind-PCBs) in egg and egg products in Turkey

Burcu Olanca *, Gul Celik Cakirogullari, Yunus Ucar, Dursun Kirisik, Devrim Kilic

National Food Reference Laboratory, Fatih Sultan Mehmet Bulv., N:70, 06170 Yenimalle, Ankara, Turkey

HIGHLIGHTS

- We analysed PCDD/Fs, dl-PCBs, ind-PCBs in egg, pasteurized egg, egg yolk powder.
- All results are below the values imposed in Turkish Regulation.
- 2,3,4,7,8-PeCDF, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, PCB126 are the most dominants.
- Daily exposure to PCDD/Fs and dl-PCBs is 0.011 pg WHO-TEQ$_{(2005)}$ d^{-1} kg bw^{-1}.

ARTICLE INFO

Article history:
Received 18 January 2013
Received in revised form 14 August 2013
Accepted 19 August 2013
Available online 19 September 2013

Keywords:
Polychlorinated dibenzo-p-dioxins/furans
Polychlorinated biphenyl
Egg
Turkey

ABSTRACT

The aim of the study is to determine concentrations of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), dioxin-like polychlorinated biphenyls (dl-PCBs) and indicator PCBs (ind-PCBs) in eggs from cage hens without soil contact, pasteurized egg samples and imported egg yolk powder samples in Turkey. Concentrations of PCDD/Fs, PCDD/Fs and dl-PCBs, and ind-PCBs in eggs and pasteurized egg samples are in the range of 0.247–1.527 pg WHO-TEQ$_{(2005)}$ g^{-1} fat, 0.282–1.762 pg WHO-TEQ$_{(2005)}$ g^{-1} fat and 202–1235 pg g^{-1} fat, respectively. For egg yolk powder samples, concentrations of PCDD/Fs, PCDD/Fs and dl-PCBs, and ind-PCBs are in the range of 0.122–0.494 pg WHO-TEQ$_{(2005)}$ - g^{-1} fat, 0.214–0.640 pg WHO-TEQ$_{(2005)}$ g^{-1} fat and 217–1498 pg g^{-1} fat, respectively. All results for PCDD/Fs, PCDD/Fs and dl-PCBs, and ind-PCBs are below the values of 2.5 pg WHO-TEQ$_{(2005)}$ g^{-1} fat, 5.0 pg WHO-TEQ$_{(2005)}$ g^{-1} fat and 40 ng g^{-1} fat imposed in Turkish Regulation for eggs and egg products, respectively. In all samples 2,3,4,7,8-PeCDF, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD and PCB126 are the most prominent congeners. Mean estimated daily exposure to PCDD/Fs and dl-PCBs for Turkish population from egg is 0.011 pg WHO-TEQ$_{(2005)}$ d^{-1} kg body weight $(bw)^{-1}$. Although the exposure levels are below the TDI of 2 pg WHO-TEQ$_{(1998)}$ kg bw^{-1}, the results were based only on consumption of egg. In order to estimate total dietary intake for Turkish population, various food items should be investigated.

1. Introduction

The term "dioxin" generally refers to the polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar polychlorinated biphenyls (PCBs) with similar biological and toxicological properties, which are liphophilic contaminants and concentrate in lipids of biological systems (Fries, 1995). Major sources of PCDD/Fs are emissions from industrial chlorination processes and combustion of materials in the presence of chlorine such as waste incineration, metal industry, chemical production, forest fires and volcanic eruptions (USEPA, 2000; EC, 2006). PCBs are man-made products used as dielectrical fluids, non-flammable oils and plasticizers in some industrial applications (Safe 1992; Ahlborg et al., 1994). Although the use and production of PCBs have been banned in most developed countries since the 1970s, they still exist in the environment (Fries, 1995; Voorspoels et al., 2008).

PCDD/Fs and PCBs have various toxic effects on immune, nervous, endocrine and reproductive systems, and potential carcinogenic effects. 2,3,7,8-TCDD, the most toxic congener of the dibenzo-p-dioxins, is classified as a Group 1 carcinogen by The International Agency for Research on Cancer (IARC) (Kodavanti et al., 1998; WHO, 1999). A tolerable daily intake of 2 pg WHO-TEQ$_{(1998)}$ d^{-1} kg body weight $(bw)^{-1}$ for dioxins and dioxin-like PCBs has been set by the EU Scientific Committee on Food (SCF) (EC, 2001).

Food is the primary source of human exposure to PCDD/Fs and dl-PCBs, contributing over 90% of total exposure (Fries, 1995; Liem

* Corresponding author. Tel.: +90 312 3274181; fax: +90 312 3274156.
E-mail address: olanca@gmail.com (B. Olanca).

0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.08.056

et al., 2000). The dioxin contaminations at lower levels of feed chain such as animal feed, pastures and organisms lead to bioaccumulation of dioxins in animal fat (Menotta et al., 2010). In 1999, Belgium had a dioxin crisis caused by dioxin contaminated feed. The source of the contamination was a fat rendering company, where transformer oil with high levels of polychlorinated biphenyls (PCBs) and dioxins was used to manufacture animal foods. Products (meat, eggs, mayonnaise, custards, cakes, etc.) with excessive levels were destroyed, including some 2 million chickens (Erickson, 1999; Van Larebeke et al., 2001). In Germany, dioxin contamination in feed causing contamination of poultry meat and eggs was reported in 2010 by RASFF (EC, 2011a).

Egg is one of the most consumed foods worldwide. It is a rich source of proteins and is known to contain essential unsaturated fatty acids, iron, phosphorus, trace minerals, the fat soluble vitamins A, D, E and K and many of the water soluble B vitamins. Egg is important in food industry due to its biological functions on humans and functional properties in foods such as noodles, mayonnaise, salad dressings, sauces, cakes and candy. As egg yolk is high in lipid (66%, dry basis), unlike the egg white which consists trace amount of fat, dioxins are likely to accumulate in the fat of yolk (Stadelman and Cotterill, 1995; Kim et al., 2009; FAO, 2010).

In European countries, the estimated contribution of egg to the total dioxin intake from food generally ranges from 2% to 5% (Harrison et al., 1998; Kiviranta et al., 2001; Baars et al., 2004; Bocio and Domingo, 2005). In the U.S. estimated daily intake of PCDD/Fs and dl-PCBs from egg is between 3.4% and 6.8% for various age groups (Schecter et al., 2001). Higher contribution (17%) from egg to dioxin intake was reported in Spain (Marti-Cid et al., 2008). Although the contribution of egg is generally calculated from intake levels of eggs commercially produced by cage hens, it is known that free-range eggs contain higher levels of dioxins (Overmeire et al., 2009). The contamination of free range hens are caused mainly by feed, emission from industry and precipitation on grassland (Menotta et al., 2010).

Although there are some studies on PCDD/Fs and PCB contaminations in foods for various countries, there is only one study from Turkey (Kilic et al., 2011). In the present study, it is aimed to determine PCDD/Fs, dl-PCBs and ind-PCBs concentrations in eggs from cities which have the highest egg production capacities in Turkey, egg yolk powder samples imported from different countries and pasteurized egg samples produced in Turkey, and compare with the other studies and legislative limit, and assess the average daily exposure.

2. Materials and methods

2.1. Materials

10 individual egg samples (12–30 eggs for each) produced commercially in cages without soil contact were collected in 2011 from the farms located in cities (Ankara, Afyon, Balikesir, Corum and Sakarya) which have the highest egg production capacities in Turkey. Egg yolk powder samples (1 kg) imported from different countries and pasteurized egg samples (1 kg) produced in Izmir and Konya were obtained from food industry in Turkey in 2011–2012. Samples were kept in refrigerator temperature (0–4 °C) until analysis.

2.2. Methods

2.2.1. Standards and solvents

All standards (EDF-7999, TCDD/F-OCDD/F; EDF-8999, ^{13}C-TCDD/F-OCDD/F; EC-4986, Non-ortho PCBs; EC-4987, Mono-ortho PCBs; EC-5179, Indicator PCBs; EC-4187, ^{13}C-NO-PCBs; EC-4188, ^{13}C-MO-PCBs; EC-4058, ^{13}C-Ind-PCBs; ED-911, ^{13}C-1,2,3,4-TCDD; ED-996, ^{13}C-1,2,3,7,8,9-HxCDD; ED-907, $^{37}Cl_4$-2,3,7,8-TCDD) were purchased from Cambridge Isotope Laboratories. 7-point calibration curve was used for quantitative measurements of PCDD/Fs. Concentrations of standards 1, 2, 3, 4, 5, 6 and 7 were 0.02, 0.10, 0.20; 0.05, 0.25, 0.50; 0.10, 0.5,1.0; 0.2, 1.00, 2.0; 0.5, 2.50, 5.0; 1.0, 5.0, 10.0 and 2.0, 10.0, 20.0 pg μL^{-1} for tetra-;penta-, hexa-, hepta-; octa-CDD/Fs congeners, respectively. 8-point calibration curve was used for determination of non-ortho, mono-ortho and ind-PCBs. Concentrations of the standards 1, 2, 3, 4, 5, 6, 7 and 8 were 0.10, 0.25, 0.50, 1.00, 2.50, 5.0, 10.0, 50.0 pg μL^{-1} for all congeners of non-ortho, mono-ortho and ind-PCBs. ^{13}C-labelled internal (2.0 pg μL^{-1} of mono-ortho and ind-PCBs; 0.10 pg μL^{-1} of PCDD/Fs; 0.20 pg μL^{-1} of non-ortho PCBs), recovery (10 pg μL^{-1} of ^{13}C-1,2,3,4 TCDD and ^{13}C-1,2,3,7,8,9 HxCDD for fraction B, and 5 pg μL^{-1} of ^{13}C-1,2,3,4 TCDD for fraction A) and clean-up (1.0 pg μL^{-1} of $^{37}C_4$-2,3,7,8 TCDD) standards were added to all calibration standards. All the solvents (n-pentane, hexane, dichloromethane, ethylacetate, toluene, isooctane) used were gas chromatography grade.

2.2.2. Extraction

8–10 egg yolks from individual egg samples were separated and homogenized. After homogenization, samples were mixed with anhydrous sodium sulphate and re-homogenized. The homogenate was mixed with 300 mL n-pentane and poured through a funnel filled with glasswool and anhydrous sodium sulphate fitted to a flask. The last step was repeated twice. The solvent was evaporated via a rotary evaporator (60 °C) and the flask left in an oven at 60 °C overnight. Pasteurized egg samples (100 g) were also extracted as mentioned above for egg samples. Egg yolk powder samples (100 g) were directly mixed with 300 ml n-pentane and poured through a funnel filled with glasswool and anhydrous sodium sulphate fitted to a flask. The last step was repeated twice. The solvent was evaporated via a rotary evaporator (60 °C) and the flask left in an oven at 60 °C overnight (Traag et al., 2006).

2.2.3. Clean-up and preparation for instrumental analysis

After obtaining fat from samples with extraction, 2.5 g of fat was pasteur-pipetted to a measuring cylinder. n-hexane was added to final volume (25 mL). Since average fat contents of egg and egg yolk powder samples are approximately 10% and 60% (Stadelman and Cotterill, 1995) respectively, and the results are expressed on fat basis, ^{13}C-labelled dioxin and PCB internal and clean-up standards were added at this step.

A Power-Prep™ system was used (Fluid Management Systems Inc., Waltham, MA, USA) for purification of PCDD/Fs, dl-PCBs and ind-PCBs. In the system, all samples were treated with the jumbo acidic silica, silica (acidic and basic layers), alumina and carbon columns (Focant et al., 2005). For elution of the columns, hexane, hexane/dichloromethane (1:1, v/v), ethylacetate/toluene (1:1, v/v) and toluene were used (Traag et al., 2008). At this step, all mono-ortho and ind-PCBs were collected initially in fraction A, and the non-ortho PCB and PCDD/Fs congeners were collected in fraction B.

The solvents were evaporated to dryness for fraction B and to 0.5 mL for fraction A in a TurboVap system. n-Hexane were added to the TurboVap tubes and then re-pipetted to smaller tubes. These tubes were concentrated to dryness under a gentle nitrogen stream in the heating mantle. Labelled recovery standards, 10 μL from the standard with a concentration of 10 pg μL^{-1} ^{13}C-1,2,3,4-TCDD and ^{13}C-1,2,3,7,8,9-HxCDD for fraction B, and 200 μL from the standard with a concentration of 5 pg μL^{-1} ^{13}C-1,2,3,4-TCDD for fraction A, were added to the tubes. After vortexing, they were pipetted into insert vials fitted in 2-mL vials to be injected into the high