Chemosphere 91 (2013) 179–186

Contents lists available at SciVerse ScienceDirect

Chemosphere

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

# Content of polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin-like polychlorinated biphenyls in fish from Latvian lakes

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## HIGHLIGHTS

- Levels of PCDD/PCDFs and dl-PCBs in freshwater fish from Latvian lakes were represented.
- Congener profiles of PCDD/PCDFs and dl-PCB were compared for freshwater fish from Latvian lakes and wild Baltic salmon.
- The daily intake of PCDD/PCDFs and dl-PCBs by freshwater fish consumption for typical Latvian was presented.

## ARTICLE INFO

*Article history:*
Received 23 May 2012
Received in revised form 30 November 2012
Accepted 15 December 2012
Available online 18 January 2013

*Keywords:*
PCDD/PCDFs
Dioxin-like PCBs
Freshwater fish
Latvian lakes
POPs

## ABSTRACT

Seventeen polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDFs) of the highest priority as well as twelve dioxin-like polychlorinated biphenyls (dl-PCBs) were analyzed in the muscle tissues of the following freshwater fish species sampled from eleven Latvian freshwater lakes: perch (*Perca flavescens*), carp (*Cyprinus carpio*), eel (*Anguilla rostrata*), bream (*Abramis brama*), chub (*Leuciscus cephalus*), pike (*Esox lucius*), sheatfish (*Silurus glanis*) and roach (*Rutilus*). To analyze the selected persistent organic pollutants in fish matrices, an optimization of EPA-1613 and EPA-1668A clean-up procedures was carried out, followed by validation of the analytical procedure according to Commission Regulation (EC) No 1883/2006. The adopted analytical procedure was in compliance with requirements of the more recent Commission Regulation (EU) No 252/2012. Modifications of carbon column chromatography clean-up and separation steps were used for treatment of the fish samples. Other clean-up procedure stages were performed according to the methods EPA-1613 and EPA-1668A and involved gel permeation chromatography (GPC), as well as manual acidic silica and Florisil column chromatography for purification and fractionation of the samples. An isotope dilution method was used for the qualitative and quantitative determination of individual congeners. Analytes of interest were separated and detected using gas chromatography – high resolution mass spectrometry. The concentration of PCDD/PCDFs and dl-PCBs in freshwater fish and eel samples ranged from 0.05 to 8.0 pg WHO(1998)-PCDD/PCDF-PCB-TEQ $g^{-1}$ fresh weight. These levels are below the EU maximum permissible limits although calculation of the content of these compounds relative to the weight of fat shows contamination levels similar to those found in Baltic herring and sprats, that are known to be highly contaminated. A difference in congener pattern between the Baltic Sea fish and freshwater fish was detected with lower contribution of 2,3,4,7,8-PeCDF to the contamination of inland water fish.



## 1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like biphenyls (dl-PCBs) are well-known persistent organic pollutants found in almost every environmental matrix. These three classes of chemically and structurally related polychlorinated aromatic hydrocarbons differ according to the number and position of chlorine atoms in the chemical structure. These groups consist of 75, 135 and 209 individual congeners, respectivelly (Gilpin et al., 2003). PCDD/PCDFs and dl-PCBs are highly lipophilic compounds with low biodegradability and high metabolic persistence. Polychlorinated dibenzo-p-dioxins, furans and biphenyls tend to accumulate in the food chain and more than 90% in dioxin-like contaminants for humans are ingested via food. Dioxin-like compounds can induce various toxic responses including immunotoxicity, carcinogenicity and adverse effects on reproduction, development, and endocrine functions (Gilbertson et al., 1991). To reduce the risk of PCDD/PCDFs and dl-PCBs exposure

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http://dx.doi.org/10.1016/j.chemosphere.2012.12.041

on human health the Commission Regulation (EC) No 1881/2006 (EC No. 1881/2006, 2006) establishes maximum levels for these contaminants in foodstuffs, expressed in World Health Organization (WHO) toxic equivalents (TEQ) using the WHO(1998)-TEF (toxic equivalency factors) (Van den Berg et al., 1998). In 2005 WHO changed a number of TEF values according to new toxicological data, notably for PCBs, octachlorinated congeners and pentachlorinated dibenzofurans (Van den Berg et al., 2006). According to these changes, the maximum levels for PCDD/PCDFs and dioxin-like PCBs were reviewed in 2011 by the Commissison Regulation (EU) No 1259/2011 using the WHO(2005)-TEF (EU No 1259/2011, 2011).

The main sources of environmental contamination of the Baltic region with PCDD/PCDFs and dl-PCBs are combustion-related processes and byproducts of pulp and paper bleaching industry (Helkom, 2004). Fish is known to accumulate lipophilic environmental organochlorine pollutants (Ministry of Agriculture, 1999) and certain aspects of the human diet in Latvia show the significant role of fish as well as fish products in the food basket (Joffe et al., 2009; Ozolins et al., 2011). There are many studies on determination of PCDD, PCDF and dl-PCB content in Baltic Sea fish species, where the results show high levels of pollutants in saltwater fish from the Baltic region (Kiviranta et al., 2002, 2003; Shelepchikov et al., 2008). However, there are no significant data on PCDD/PCDF and dioxin-like PCB content in freshwater fish sampled from Latvian freshwater lakes. To gain an overview of the actual contamination level with polychlorinated dibenzo-p-dioxins and furans, as well as with dl-PCBs in Latvian freshwater fish, a monitoring program was implemented using fish samples from eleven different freshwater lakes and the results are presented in this paper.

## 2. Materials and methods

### 2.1. Sample collection and storage

Eleven fish species were collected in Latvian freshwater lakes, at the sampling locations shown in Fig. 1. To get an overview of the actual contamination levels of PCDD/PCDFs and dl-PCBs in freshwater fish species, sampling locations were selected to evenly cover all territory of Latvia. At least five specimens of each fish species were collected. Samples were packed in polyethylene bags and stored with ice during the delivery to the laboratory. Upon receiving at the laboratory, a unique code was given to each sample. To obtain a representative sample after the cutting and pooling of fish fillets, the material was homogenized in a food blender (Kenwood FP101T, Kenwood Ltd., UK), packed in polyethylene bags and stored at −18 °C until analysis. An appropriate sample amount (50–60 g) was analyzed for each of the 17 PCDD/PCDFs and 12 dl-PCBs, for which the WHO (Van den Berg et al., 1998, 2006) has developed toxicity equivalency factors (TEFs).

### 2.2. Chemicals and materials

All solvents (hexane, toluene, dichloromethane, cyclohexane and ethylacetate) were pesticide grade and purchased from LabScan (Glivice, Poland). Silicagel (Kieselgel 60, 0.063–0.200 mm), Florisil, Celite-545 and Carbopack B were obtained from Sigma–Aldrich Chemie GmbH (Buchs, Switzerland), sulfuric acid and sodium sulfate were obtained from Acros (New Jersey, USA). Calibration kits EDF-9999 and EC-4976, $^{13}C_{12}$ – labeled congener solutions EDF-8999 and EC-4937, and recovery standard solutions EDF-5999 and EC-4979 were purchased from Cambridge Isotope Laboratories, Inc. (Andover, USA).

### 2.3. Instruments

For the removal of high molecular mass compounds, a gel permeation chromatography system was used (model *O-I-Analytical,* Texas, USA), for additional clean-up steps a preparative chromatography system for carbon columns (controller 600; autosampler 717 plus; fraction collector III; Waters, Milford, USA) was employed.

Detection and quantitation of PCDD/PCDFs and PCBs was performed using a capillary gas chromatograph (model 6890N, Agi-


**Fig. 1.** The location of freshwater fish sampling throughout Latvia.