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Identification of Baltic Sea salmon based on PCB and dioxin profiles

Søren Sørensen [a], Kirsten H. Lund [a], Tommy L. Cederberg [b], Nicolai Z. Ballin [a, *]

[a] Danish Veterinary and Food Administration (DVFA), Søndervang 4, DK-4100 Ringsted, Denmark
[b] National Food Institute, Technical University of Denmark, Mørkhøj Bygade 19, DK-2860 Søborg, Denmark

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ABSTRACT

Salmon and herring from the Baltic Sea are prohibited for sale for human consumption in the European Union or only allowed to be marketed under certain conditions. Fish from certain specific geographical origins also command higher prices in the market than fish from elsewhere. It is, therefore, important to be able to enforce correct labeling of geographical origin through authentication. One authentication strategy is to examine trace markers specific for a geographical origin. The chemical contaminants polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) were released inhomogeneously into the environment for many years and may therefore be suitable as markers. This study comprises PCBs and PCDD/Fs analyses of 79 samples of salmon originating from Canada, Chile, China, Norway, USA, Vietnam, and the Baltic Sea near Denmark, all sampled from 2002 through 2015. Principal component analyses (PCA) were built from the combined PCB and PCDD/F profile as well as separately from the individual PCB and PCDD/F profiles. Use of the PCB profile for the PCA provided stronger power to distinguish between salmon of different geographical origin than using the PCDD/F profile or the combined profiles.

1. Introduction

Persistent organic contaminants such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) have attracted special attention as they have caused several serious food and feed contamination incidents in the 1990s (Malisch & Kotz, 2014). From 1929, PCB mixtures were manufactured for various industrial purposes including use as flame-retardants, heat transfer fluids, hydraulic fluids, and plasticizers (Erickson & Kaley, 2011), until a ban of use and marketing was adopted in European legislation in 1985 (Erickson & Kaley, 2011; Malisch & Kotz, 2014). Before this ban, the release of PCBs into the environment varied, depending on production sites, industrial use, dumping grounds etc. Nowadays, products that contain PCBs are still present in both industrial equipment and in private households despite their discontinued industrial use. A continuous release of PCBs into the environment is, therefore, inevitable and will occur geographically inhomogeneously. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) generally known as dioxin are formed through chlorine bleaching, combustion processes, metals smelting and refining as well as from natural sources and as byproducts from chemical manufacturing. The sources of PCDD/F and its release from environmental reservoirs vary accordingly (U.S. Environmental Protection Agency, 2006). Both PCBs and PCDD/Fs are toxic lipophilic compounds that bioaccumulate along the food chain.

The bioaccumulation of PCBs and PCDD/Fs is particularly significant in predators and in animals with a high fat content. Fatty fish, including salmon, herring, sprat, and eel were subjected to several recent studies concerning their PCB and PCDD/F congener content (Blanchet-Letrouvé et al., 2014; Shelepchikov et al., 2008; Szlinder-Richert, Barska, Usydus, Ruczynska, & Grabic, 2009; Vuorinen et al., 2012; Zacs, Bartkevics, & Viksna, 2013). Not surprisingly, the contamination of these fish with PCB and PCDD/F congeners varies with the geographically inhomogeneous contamination of the environment (Hites et al., 2004; Iannuzzi, Huntley, Bonnevie, Finley, & Wenning, 1995; Isosaari et al., 2006; Verta et al., 2007). The semi-enclosed Baltic Sea of 370.000 km^2, surrounded by highly industrialized countries, is one of the most contaminated environments in the world (Shelepchikov et al., 2008; Verta et al., 2007; Wiberg et al., 2013). Because of the high levels of PCB and PCDD/F congeners in salmon from the Baltic Sea, a series of different restrictions on trade of

* Corresponding author.
E-mail addresses: nixb@fvst.dk, nicolaiba@hotmail.com (N.Z. Ballin).

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Abbreviations

GC	gas chromatography
HxCDD/F	hexachloro dibenzo-*p*-dioxin and furan
HpCDD/F	heptachloro dibenzo-*p*-dioxin and furan
ICES-6 PCBs	International Council for the Exploration of the Sea's 6 indicator PCBs
ML	maximum levels
MS	mass spectrometry
OCDD/F	octachloro dibenzo-*p*-dioxin and furan
PC	principal component
PCA	principal component analysis
PCB	polychlorinated biphenyl
PCDD/F	polychlorinated dibenzo-*p*-dioxins and furans especially the 2,3,7,8-chloro substituted
PeCDD/F	pentachloro dibenzo-*p*-dioxin and furan
TCDD/F	tetrachloro dibenzo-*p*-dioxin and furan
TEF	toxic equivalent factor
TEQ	toxic equivalents
WHO	World Health Organization

salmon as food were introduced in the countries surrounding the sea. Additionally, the European Union has regulated the maximum levels of PCBs and PCDD/Fs (European Commission, 2011) in certain fish, and provided methods for sampling and analysis for use in official control (European Commission, 2014). A Danish national provision on prohibition of sale for human consumption of salmon and herring caught in the Baltic Sea (Retsinformation, 2011), describes that salmon caught in the Danish fishing area (ICES subdivision 24–32) can only be commercially distributed for human consumption if the cleaned weight of the fish does not exceed 5.5 kg, and salmon weighing between 2.0 and 5.5 kg must be fat trimmed before being put on the market. When the distribution of salmon from specific geographical areas is restricted, authentication measures must be in place for control purposes. Effective control of potentially illegal salmon from the Baltic Sea calls upon special attention to avoid this product finding its way to the European market. Information about such fraudulent practice is not systematically collected in the EU system; however, one notification was recently reported in the Rapid Alert System for Food and Feed (RASFF, 2013). Furthermore, salmon from some geographical areas command a higher price in the marketplace than salmon from other geographical areas, which provides an economic incentive for mislabeling salmon with information about their geographical origin. Worldwide estimates of illegal and unreported catches of fish range from 4 to 34% of the total catch depending on region, and with an estimated value of $10 to $23.5 billion/year (Agnew et al., 2009). The above shows the importance of implementing geographical authentication measures for control purposes.

Authentication of geographical origin of salmon has been shown with meristic and morphometric characters (MacCrimmon & Claytor, 1985), genetic signatures (Griffiths et al., 2010), and nuclear magnetic resonance (NMR) (Aursand et al., 2009). This study investigates if principal component analysis (PCA) of the profile of PCB and PCDD/F congeners can identify salmon from the Baltic Sea and perhaps can discriminate between salmon from other geographical origins. The present study includes the analysis of 79 wild, farmed, raw, and smoked samples of salmon originating from a range of countries and collected from 2002 through 2015.

2. Materials and methods

2.1. Samples

79 samples of salmon originating from Canada (n = 1), Chile (n = 6), China (n = 2), the Baltic Sea (n = 47), Norway-1 (n = 12), Norway-2 (n = 7), USA (n = 3), and Vietnam (n = 1) were sampled from 2002 through 2015. The seven samples here labeled Norway-2 lacked clear information about geographical origin; however, they were expected to originate from Norway because the vast majority of commercially available salmon on the Danish retail market originates from Norway (The Danish AgriFish Agency, 2013), see further discussion in Results and Discussion section. In the following, Norway-1 and Norway-2 are collectively referred to as Norway. All sampled fish originated from the species within the subfamily of *Salmonidae*. Moreover, fish from the Baltic Sea and from Norway were labeled as being of the species of *Salmo salar*. The samples from the Baltic Sea originated from a Danish surveillance program that investigated the levels of the PCB and PCDD/F congeners in different sizes of salmons. All other fish samples were intended for human consumption in Denmark and sampled at border controls or in retail. In order to build a robust geographical discrimination model, salmon of different species, size, and age, as well as wild, farmed, raw, and smoked salmon were included, see Table 1.

All Baltic Sea samples were from the fishing area of ICES subdivision 25 and were pools of 5–10 fish. Pools were established according to weight in 7 groups ranging from 2 to 12 kg. The other samples were pools consisting of 1–5 whole fish or fish parts sold on the Danish market. Fillets without skin were homogenized and kept at −20 °C until chemical analysis. Samples were generally stored for a maximum of one month prior to analysis.

2.2. PCB and PCDD/F

The PCB analysis included the 4 non-ortho PCBs, the 8 mono-ortho PCBs with an assigned toxic equivalent factor (TEF), the ICES-6 PCBs, and the PCB170. The PCDD/F analysis included the 7 PCDDs and the 10 PCDFs with an assigned TEF (Van den Berg et al., 2006).

2.3. Analysis

The Commission Regulation 589/2014 (European Commission, 2014) that lay down the requirements for the analysis of PCBs and PCDD/Fs was followed. In brief, 5–12 g of homogenized fish was dried in a microwave oven for 2 min and then used for accelerated solvent extraction on an ASE300 (Dionex) using acetone/pentane (12/88). Prior to 2011, microwave drying was not used. The samples were spiked with the corresponding ^{13}C-labeled internal standards for all PCBs and PCDD/Fs. The amount of extracted fat was determined gravimetrically. The extracted fat was dissolved in hexane and further cleanup and fractionation was performed on a PowerPrep system (FMS, USA). The following procedure was based on the method by Focant et al. (Focant, Eppe, Pirard, & De Pauw, 2001). Two fractions were collected: A fraction containing the 17 PCDD/Fs and the 4 non-ortho PCBs, and a fraction containing the 8 mono-ortho PCBs, the ICES-6 PCBs, and the PCB170. A gas chromatograph coupled to a high-resolution sector mass spectrometer (Trace GC ultra and Finnigan MAT95) with electron ionization was used for detection. The mass spectrometer had a resolution of at least 10,000 and selective ion monitoring (SIM) was used. The TargetQuan software (ThermoFinnigan, Germany) was used for the quantification. All contents of congeners were calculated as upper bound values, *i.e.* non-detects were set equal to the quantification