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Perfluoroalkyl acids in various edible Baltic, freshwater, and farmed fish in Finland

Jani Koponen[a,*], Riikka Airaksinen[a], Anja Hallikainen[b], Pekka J. Vuorinen[c], Jaakko Mannio[d], Hannu Kiviranta[a]

[a] National Institute for Health and Welfare, Department of Environmental Health, Kuopio, Finland
[b] Finnish Food Safety Authority Evira, Helsinki, Finland
[c] Finnish Game and Fisheries Research Institute, Helsinki, Finland
[d] Finnish Environment Institute, Helsinki, Finland

HIGHLIGHTS

- Domestic Baltic and freshwater fish are a source of PFAAs in the Finnish diet.
- Total PFAA concentration in the Baltic and freshwater fishes varied from 0.31 to 46 ng g^{-1} fresh weight.
- Farmed fish in Finland is not a significant dietary source of PFAA for humans.
- PFAA levels in a single fish species are not representative of the PFAA contamination in a given area.

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ABSTRACT

In this study, the concentration of perfluoroalkyl acids (PFAAs) in various edible Finnish Baltic Sea, freshwater, and farmed fish species were analysed. PFAAs were present in all the Baltic and freshwater species, but were not observed in any farmed fish. The most abundant compound in each species was perfluorooctane sulfonate (PFOS), comprising 41–100% of the total concentration. The total PFAA concentration varied considerably from 0.31 to 46 ng g^{-1} fresh weight. A notable variation in the PFAA concentrations implies that a single fish species alone is not suitable for monitoring PFAA contamination in a certain area. Our results confirm that wild domestic fish is one of the PFAA source in the Finnish diet.

1. Introduction

Perfluoroalkyl acids (PFAAs), including perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS), are a subgroup of per- and polyfluorinated alkyl substances (PFAS). These substances have been widely used in many industrial and commercial applications (Buck et al., 2011). Since the carbon–fluorine bond is extremely strong and stable some of these compounds are chemically and biologically inert. However, these properties are highly related to the molecular weight and number of C–F bonds of the compound (Buck et al., 2011). Although the PFAAs are persistent, a bioaccumulative potential of the compounds is highly dependent on a chain length of the fluorinated carbons, Perfluorinated carboxylates with seven fluorinated carbons or less are not bioaccumulative according to regulatory criteria (Conder et al., 2008). PFAAs are ubiquitous in the environment and present in both environmental and human matrices (Fromme et al., 2009). The use of PFOS has been limited in EU-legislation almost a decade ago (directive 2006/122/EC) and its use in water resistant consumer products will be reconsidered again in 2015.

Abbreviations: fw, fresh weight; LC–ESI–MS/MS, liquid chromatography electrospray tandem mass spectrometry; LOQ, limits of quantification; PFAA, perfluoroalkyl acid; PFAS, per- and polyfluorinated alkyl substances; PFOS, perfluorooctane sulfonic acid.

* Corresponding author. Address: P.O. Box 95, FI-70701 Kuopio, Finland. Tel.: +358 29 524 6350; fax: +358 29 524 6499.
E-mail address: jani.koponen@thl.fi (J. Koponen).

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Compounds in many classes of environmental pollutants have been associated with adverse health effects. PFAS may increase total and LDL cholesterol and the risk of breast cancer (Nelson et al., 2009; Steenland et al., 2009; Frisbee et al., 2010; Bonefeld-Jorgensen et al., 2011). Dietary intake is believed to be the major exposure route for PFAAs in the general adult population (Fromme et al., 2009; Haug et al., 2011; Vestergren et al., 2012).

The Baltic Sea is highly susceptible to pollution because it is a closed sea area with little water exchange with the North Sea, and because of its large catchment area with a population of about 85 million people and a high number of pollutant sources. The environmental pollutant levels in Baltic fish are often higher than in larger water bodies such as the Atlantic and Pacific oceans (Burreau et al., 2006). In Baltic herring and salmon (Isosaari et al., 2006; Szlinder-Richert et al., 2009; Airaksinen et al., 2014), the levels of pollutants, such as dioxins and PCBs, occasionally exceed the legal maximum levels for fish set by EU (1258/2011). Fish and seafood have been found to be one of the major sources of human dietary exposure to PFAAs in the Nordic diet (Haug et al., 2010b; Vestergren et al., 2012). Yearly consumption of a domestic fish in Finland has been estimated to be 3.8 kg per person, including Baltic herring (0.3 kg), pike–perch (0.3 kg), perch (0.5 kg), whitefish (0.2 kg), vendace (0.6 kg) and farmed rainbow trout (1.0 kg) (FGFRI, 2012).

The main objective of this study was to collect data about PFAA concentrations in fish commonly consumed in Finland for future dietary intake and human exposure assessments, and to investigate possible correlations between PFAA concentrations and selected physiological parameters in fish. In the future, this data can be utilized as a reference data for the measures taken in the follow up and monitoring of contaminated Baltic Sea fish.

2. Materials and methods

2.1. Sampling and preparation

The species collected from the Baltic Sea were Baltic herring (*Clupea harengus*), pike–perch (*Sander lucioperca*), perch (*Perca fluviatilis*), burbot (*Lota lota*), whitefish (*Coregonus lavaretus*), salmon (*Salmo salar*), and vendace (*Coregonus albula*). In addition, perch and pike–perch were collected from Helsinki Vanhankaupunginlahti bay, and perch was collected from Lake Päijänne. Farmed fish species included in this study were whitefish and rainbow trout (*Oncorhynchus mykiss*) (Table 1). The selection of fish species was mainly based on the significance of fish in the Finnish diet.

Altogether 296 individual fish samples were collected in 2009–2010 from five commercially and recreationally important fishing areas across the Finnish coast of the Baltic Sea (areas nearby the cities of Oulu, Pori, Turku, Hanko, and Kotka), Helsinki Vanhankaupunginlahti bay, a large freshwater Lake Päijänne, and four fish farming facilities (Fig. 1). Most of the individual samples were pooled. The pooled samples consisted of 2–10 individuals. Fish age was determined in scale or appropriate bony structure.

The samples were frozen until preparation. From the large fish, a medallion was cut from around the dorsal fin and for small fish, the head was removed. Intestine and skin were removed, and meat and subcutaneous fat were homogenized to form a pooled sample according to EU directive 1883/2006. The homogenized fish samples were freeze-dried and stored frozen until PFAA analysis.

2.2. Chemicals and reagents

Methanol (HPLC grade) and ammonium acetate were obtained from J.T. Baker (Deventer, the Netherlands), and N-methylpiperidine from Sigma–Aldrich (St. Louis, MO, USA). All the native PFAAs, i.e. perfluorohexanoic acid (PFHxA), -heptanoic acid (PFHpA), -octanoic acid (PFOA), -nonanoic acid (PFNA), -decanoic acid (PFDA), -undecanoic acid (PFUnA), -dodecanoic acid (PFDoA), -tridecanoic acid (PFTrA), -tetradecanoic acid (PFTeA), -hexanesulfonate (PFHxS), -heptanesulfonate (PFHpS), -octanesulfonate (PFOS) and -decanesulfonate (PFDS) were acquired from Wellington Laboratories Inc (Guelph, Ontario, Canada). Isotope labelled PFAAs (abb. MPFAA) were used as internal standards. MPFOA (1,2,3,4-$^{13}C_4$), MPFNA (1,2,3,4,5-$^{13}C_5$), MPFUnA (1,2,3,4,5,6,7-$^{13}C_7$), MPFDoA (1,2-$^{13}C_2$), MPFHxS ($^{18}O_2$) and MPFOS (1,2,3,4-$^{13}C_4$) were obtained from Wellington Laboratories Inc. and MPFDA (1,2,3,4,5,6,7,8,9-$^{13}C_9$) was from CIL (Andover, MA, USA).

2.3. PFAA analysis

For quantitation prior to an extraction procedure a 2.5 ng of mass labelled internal standards in 50 μL of methanol were added into 0.3 g of freeze-dried fish samples. The samples were extracted twice with 2 mL of 20 mM ammonium acetate in methanol. After mixing for 10 min at 2500 rpm with Vibramax 110 (Schwabach, Germany), the samples were centrifuged with Eppendorf 5810 (Hamburg, Germany) at 2500 g for 10 min. The supernatants were collected. The extracts were evaporated to dryness under a nitrogen flow and reconstituted to 300 μL of 60% aqueous methanol. Prior to instrumental analysis, the samples were filtered with 0.2 μm syringe filter (Pall Life Sciences, Ann Arbor, MI). The PFAAs were analysed using liquid chromatography negative ion electrospray tandem mass spectrometry (LC–ESI–MS/MS). Details of the

Table 1
Gender, length, weight, age, and fat percentage in Baltic, freshwater, and farmed fish.

Fishing area	Species	Region	Gender	Length (cm)	Weight (g)	Age (year)	Fat (%)
Baltic Sea	Baltic herring (*n* = 58)	Pori	Male, female	16–22	28–76	4.2–17	2.2–13
	Pike–perch (*n* = 30)	Oulu, Turku, Kotka	Male, female	37–45	420–830	3.4–7.0	0.93–3.1
	Perch (*n* = 25)	Oulu, Pori, Turku, Hanko, Kotka	Male, female	26–28	200–290	5.2–8.0	1.8–2.9
	Burbot (*n* = 49)	Oulu, Pori, Turku, Hanko, Kotka	Male, female	47–58	590–1430	3.0–5.6	0.71–0.89
	Whitefish (*n* = 27)	Oulu, Pori, Turku, Hanko, Kotka	Male, female	29–51	240–1250	2.5–6.6	2.7–6.7
	Salmon (*n* = 44)	Oulu, Pori, Turku, Hanko, Kotka	Male, female	76–94	4740–9320	1.8–2.2	13–20
	Vendace (*n* = 20)	Oulu	Female	16–17	29–36	1.8–2.0	5.1–5.4
Vanhankaupunginlahti bay	Pike–perch (*n* = 6)	Helsinki	Female	31–51	230–1110	3.0–9.0	n/a
	Perch (*n* = 7)	Helsinki	Male, female	17–22	70–130	5.0–10	n/a
Lake Päijänne	Perch (*n* = 10)	Päijänne	Male, female	20–25	87–190	8.0–10	1.2–1.8
Farmed fish	Whitefish (*n* = 10)	Northern and Southern Finland	Male, female	38–39	650–670	n/a	21–23
	Rainbow trout (*n* = 10)	Central and Southern Finland	Female	45–50	1280–1830	n/a	17–18

n = Number of individual fishes.
n/a Not analysed.