Occurrence of PFAS in a variety of fish species from the Baltic Sea and freshwater locations of Finland

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Per- and polyfluoroalkyl substances (PFAS) are a large group of fluorinated chemicals that have been widely used in industrial and consumer applications since the 1950s, owing to their water, oil, and dirt repellent properties. More than 4000 PFAS have been identified as likely available on the global market (OECD, 2018). The distribution of perfluoroalkyl acids (PFAAs), one of the sub-categories of PFAS, is ubiquitous globally in the environment and biota. PFAAs are found even in the wildlife of the Antarctica which is the most pristine continent (Garcia et al., 2022). PFAAs are chemicals of health concern because of their persistent nature, bioaccumulation potential, toxicity of certain PFAAs, and their association with adverse health effects including development effects, adverse effects on the liver, serum cholesterol and immune system (EFSA, 2020).

Due to the related concerns, production and use of specific PFAS has been restricted or strictly limited globally. Perfluorooctane sulfonic acid (PFOS) and its derivatives were listed in Annex B to the Stockholm Convention in 2009 to eliminate their use globally. In addition, perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds were listed in Annex A to the Stockholm Convention in 2020. Two PFAS groups (perfluorobutane sulfonic acid and its salts; 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid, its salts and its acyl halides) have also been identified as substances of very high concern and are on the REACH Candidate List.

The major source of PFAS exposure to the general population is diet, however, other sources such as drinking water, dust ingestion, indoor air inhalation may also contribute substantially. Fish meat, which is a vital source of protein for the world's population, is one of the main food categories contributing to the PFAA exposure for all population groups *(Figure.1)*. A new safety threshold – group tolerable weekly intake (TWI) of 4.4 ng kg^{-1} of body weight (bw) per week, which would protect adverse effects observed in humans – was derived by the European Food Safety Authority in 2020 for the four PFAS (PFOA, perfluorononanoic acid (PFNA), perfluorohexane sulfonate (PFHxS) and PFOS) that contribute most to levels observed in human serum (EFSA, 2020). Monitoring of PFAS in commercially important fish species and exposure assessment is therefore relevant with respect to dietary routes of exposure.

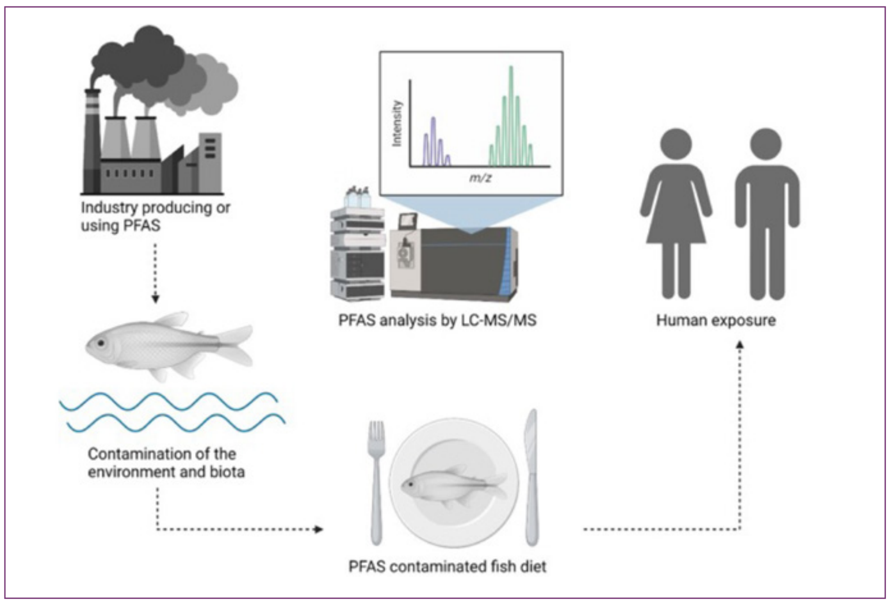

Figure.1. PFAS exposure of humans via contaminated fish consumption. Created with BioRender.com

In this regard, the Chemical Risks team at Finnish Institute for Health and Welfare (THL), in collaboration with Natural Resources Institute Finland, Finnish Environment Institute and Finnish Food Authority, has conducted extensive monitoring assessments on fish health from 2001 onwards and evaluated the concentrations of several persistent organic pollutants including PFAS in freshwater and the Baltic Sea fish and evaluated the risk posed by these pollutants to human health. The latest sampling for this monitoring programme was conducted in 2016-2017. PFAA analysis in fish was performed in the laboratory of the Chemicals Risk team at the THL, which is accredited by the Finnish Accreditation Services according to the SFS-EN ISO/IEC 17025:2017 standard. The Chemical Risks team at THL has the capacity to analyse a large variety of industrial chemicals and their by-products from various human and environmental matrices including dioxins, polychlorinated biphenyls, flame retardants, PFAS, phthalates, bisphenols.

PFAS analyses of fish from the Finnish Baltic Sea sub-basins and lakes

Fish sampling for this monitoring and assessment programme was conducted in the four Baltic Sea sub-basins (Bothnian Bay, Bothnian Sea, Archipelago Sea and Gulf of Finland) bounded by the Finnish coast and freshwater lakes (Lake Päijänne, Lake Saimaa, Lake Oulujärvi) in 2016-2017. Commercial and dietary significance were the main criteria for the selection of the fish species. 13 fish species were sampled, and a total of 1134 individual fish specimens were collected. Specific data on fish species including length, weight, age, and fat content were recorded. PFAS analysis was performed using part of the homogenates. 13 PFAAs (perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, PFNA, perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), PFHxS, perfluoroheptane sulfonate (PFHpS), PFOS, and perfluorodecane sulfonate (PFDS)) were investigated in the study samples. The PFAS analyses was performed using liquid chromatography (Dionex Ultimate 3000 RS) coupled to triple quadrupole mass spectrometry (Finnigan TSQ Quantum Discovery Max) in electrospray negative ionisation mode (LC-ESI-MS/MS). Limits of quantification for individual PFAAs ranged between 0.25 – 0.37 ng g^{-1} wet weight (ww).

PFAA concentrations in the Baltic Sea fish

Several PFAAs were detected in the fish species caught in the Baltic sub-basins. PFOS was present in at least 97% of the Baltic Sea fish samples and dominated the PFAA profile in fish, followed by PFNA and PFUnDA *(Figure. 2)*. Contribution of PFOA and PFTrDA to overall PFAA concentrations in the Baltic Sea fish species was minor. PFOA was found to be present in Baltic herring and smelt which could be explained by dietary, behavioral factors and/or species specific toxicokinetic behavior. The results of this study have been published in detail elsewhere (Kumar et al., 2021).

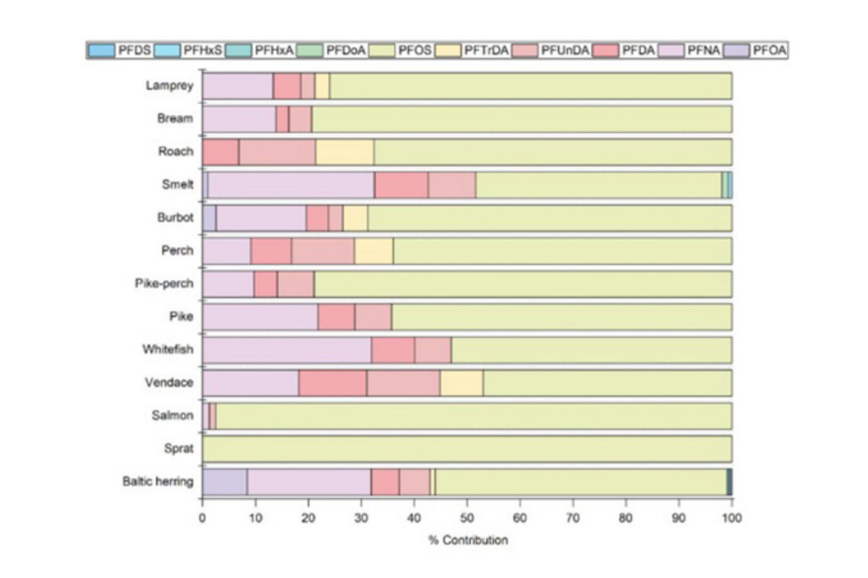

Figure. 2: Contribution (%) of individual homologues to ∑PFAA in Baltic Sea fish species. Reprinted from (Kumar et al., 2021).

The highest median ∑PFAA concentrations were observed in smelt (33.1 ng g^{-1} ww), lamprey (5.86 ng g^{-1} ww), and vendace (5.75 ng g^{-1} ww), primarily due to elevated PFOS concentrations *(Figure. 3)*. Junttila et al. (2019) have previously reported about the dominance of PFOS in fish caught in the marine and coastal areas of southern Finland. Lowest median ∑PFAA concentrations were found in roach (1.45 ng g^{-1} ww) and burbot (1.43 ng g^{-1} ww). These observations are different from those found in the previous PFAS monitoring study conducted by THL and collaborators in 2009-2010 (Koponen et al., 2015).

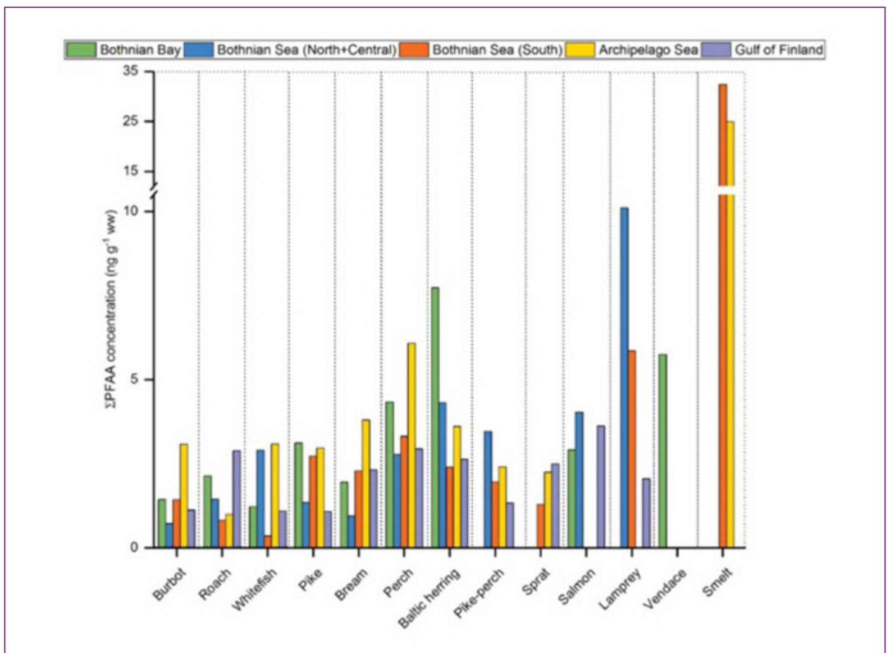

Figure. 3. Median ∑PFAA concentration (ng g^{-1} ww) grouped by species and capture location in the Baltic Sea. Reprinted from (Kumar et al., 2021).

PFAS concentrations in freshwater fish

The PFAA profile in the fish from freshwater lakes was different from that found in the Baltic Sea fish. The main homologues found in lake fish samples included PFOS, PFTrDA, PFDoDA, PFUnDA, and PFDA. The PFAA profile in lake fish was dominated by PFUnDA, PFTrDA, and PFOS *(Figure. 4)*. The highest ∑PFAA concentrations were observed in pike-perch (4.78 ng g^{-1} ww) and vendace (3.04 ng g^{-1} ww).

Concentration ratios of PFOS to other PFAAs in lake fish were dissimilar from that observed in Baltic Sea fish. This may be attributed to the difference in pollution pattern in freshwater and seawater fish species. PFOS contributes more to PFAA contamination in the Baltic Sea as compared to C9-C14 perfluoroalkyl carboxylic acids. Overall, fish from the Finnish lakes had lower ∑PFAA concentrations compared to the Baltic Sea fish.

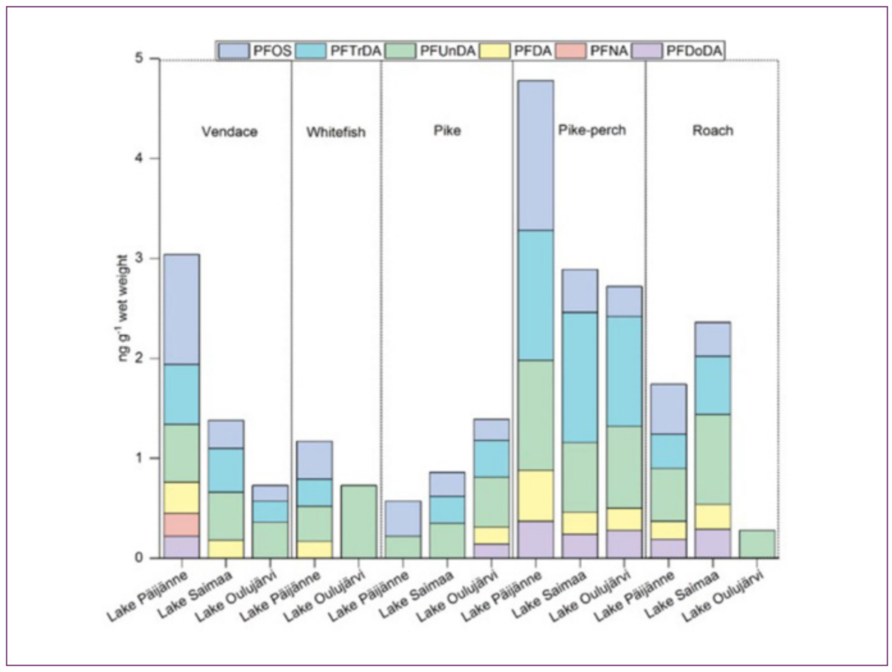

Figure 4. Median ∑PFAA concentration (ng g^{-1} ww) and corresponding PFAA homologue profiles in Finland's lake fish species. Reprinted from (Kumar et al., 2021).

PFAS exposure among Finnish consumers via fish diet

We compared the results based on PFAA concentration in fish and calculated PFAA intake with the group TWI proposed by EFSA for the sum of PFOA, PFNA, PFHxS and PFOS (∑PFAS-4 = 4.4 ng kg^{-1} bw $week^{-1}$). Mean ∑PFAS-4 concentrations varied from 1.12 ng g^{-1} ww in roach to 23.27 ng g^{-1} ww in smelt. Average consumption of wild-caught fish in Finland was 46 g $week^{-1}$ in 2018 and that of smelt was marginal (Luke, 2019). Therefore, assuming 46 g of weekly fish consumption and 70 kg body weight, the TWI would be exceeded for smelt only. Nonetheless, these findings highlight the need for environmental and human biomonitoring and demonstrates the significance of fish diet towards the total dietary PFAS intake.

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