Exposure of PFAS in food – Levels and composition

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The widespread passive distribution of per/polyfluorinated substances (PFAS) as well as the more direct exposures to humans and the environment have been studied for 25+ years. The level of knowledge has increased rapidly, but many issues remain. The picture is complex in terms of occurrence, composition and tools for risk assessment. Not at least through EFSA's (EU Food Agency) much reduced TWI (tolerable weekly intake) value for the sum of four PFASs, food has come more and more into focus. The priority substances of the water framework directive (WFD) are also being revised and a new limit (EQS) for biota (fish) of 77 ng/kg FW PFOA eqv for PFAS24 (COM(2022) 540) has been proposed. In addition, limit values for foodstuffs in EU has been enforced in 2023 ((EU) 2023/915) and also a new screening within EU has been decided ((EU) 2022/1431). This increases the relevance of food/biota monitoring and the levels can be critical both with regard to environmental and food intake assessments.

Background

PFAS are a broad group of chemicals that have been used for various purposes since the 1950s. In Sep 2020, EFSA reduced the tolerable intake value (TWI) for PFAS by approximately 240 times to 4.4 ng per kg body weight and week. Unlike before, this corresponds to the sum of four PFASs (PFOS, PFOA, PFNA and PFHxS). Since 23 EU limit values are in force for fish, meat and egg for PFAS4. There is also a screening recommendation, (EU) 2022/1431, with low action limits. Moreover, the draft WFD suggests a wider scope and a much lower EQS than before. Taken this development food/biota will become an increasingly important matrix, not only for food and environmental monitoring but also contaminated land management. The purpose of this study is to give an overview of levels and patterns, especially in fish but also other foodstuffs and relate to intake/limit values.

Material and Methods

Frozen consumer fish fillets of common species were purchased in supermarkets and an online store. Five jars of fish containing baby food were also included. As reference a sample of beef mince and two meat based baby foods were determined. Frozen whole perch from Lake Storavan in N Sweden was a kind gift from a local fisher and the fish was dissected in the lab. All foodstuffs were mixed. In total 42 PFAS were analysed comprising PFCA (14), PFSA (12), sulphonamides (SA; 5), PFEA (7) and FTSA (4) in the interval C3-C18. LOQ ranged from 1 to 100 with PFAS4 between 2-4 and most <10 ng/kg FW. Analysis was performed in duplicates and blanks plus controls were determined for each batch. Branched (Br) and linear (Lin) forms were separated and summarised when found.

Results

In total 16 of the 42 PFAS analysed could be detected (Table 1). As expected PFOS was the most common substance and in most cases also present at the highest concentration (<4-3800 ng/kg FW). All PFAS4 were identified but PFOA and PFHxS slightly less frequent. Long PFCAs (C10-14) were seen in almost all non-farmed fish at significant levels (<3-640 ng/kg FW). Overall the levels of PFAS were much lower in farmed fish and meat products. Among the precursors 6:2 FTS was occasionally seen, but PFBSA, PFHxSA and PFOSA were more common (<1-240 ng/kg FW). The C4- and C6-SA showed, with three exceptions, higher concentrations than the corresponding PFSA. For the so called "novel" PFAS none of the seven PFEA was found but the cyclic PFECHS was seen in a wild salmon. Sum of PFAS4 and PFAS TOT (all 42) ranged between n.d.-4000 and 10-6100 ng/kg FW.

Table 1. concentrations (ng/kg FW) of identified PFAS, ΣPFAS4 and WFD ΣPFAS24 (PFOA eqv), ΣPFAS TOT in **(a)** salmon, **(b)** white fish/ beef mince, **(c)** baby food

PFAS (ng/kg FW)	Salmon (n=2)	Salmon	Salmon
(a)	Norway/ Farmed	Kalix (SE)/ Wild	Vänern (SE)/Wild
PFBS	n.d	n.d.	n.d
PFBSA	4,0	190	56
PFHpA	n.d.	n.d	n.d
PFHxSA Lin+Br	2,5	11	22
PFHxS Lin+Br	n.d	80	13
PFOA Lin+Br	n.d	n.d	n.d
6:2 FTS	n.d	n.d	n.d
8:2 FTS	n.d	n.d	n.d
PFHpS	n.d	20	n.d
PFECHS	n.d	35	n.d
PFNA	n.d.	73	180
PFOS Lin+Br	5,2	2000	3800
PFOSA Lin+Br	42	30	240
PFDA	n.d	27	640
PFUdA	n.d	54	620
PFDoA	n.d	12	240
PFTrDA	n.d	17	220
PFTeDA	n.d	3	53
SUM PFAS4	5,2	2200	4000
SUM WFD prel PFAS24	10	5300	17500
SUM PFAS TOT	54	2600	6100
PFAS4/PFAS TOT (%)	13	84	66

PFAS (ng/kg FW)	Pangasius	Herring	Mackerel	Alaska pollock	Plaice	Cod (n=5)	Perch (n=3)	Norway lobster	Prawn	Beef mince
(b)	Vietnam/ Farmed	Norweg-ian Sea	Norweg-ian Sea	Pacific ocean	North Sea	NE Atlantic	Storavan (SE)	North Sea	NE Atlantic	Sweden
PFBS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d	n.d	n.d	n.d.
PFBSA	6,9	6,9	5,8	1,4	14	14	n.d	35	n.d	n.d.
PFHpA	n.d	9,0	n.d	n.d	n.d	n.d	n.d	20	n.d	n.d.
PFHxSA Lin+Br	n.d	3,6	7,5	1,2	3,8	29	n.d	34	11	n.d.
PFHxS Lin+Br	n.d	n.d	n.d	n.d	7,7	1,8	n.d	n.d	n.d	n.d.
PFOA Lin+Br	n.d	8,5	n.d	6,4	8,5	6,2	n.d	140	16	n.d.
6:2 FTS	n.d	n.d	n.d	n.d	n.d	n.d	42	n.d	n.d	24
8:2 FTS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d.
PFHpS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d.
PFECHS	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d.
PFNA	n.d	11	6,6	50	110	57	88	97	110	2,6
PFOS Lin+Br	n.d	34	56	13	630	244	170	50	280	11
PFOSA Lin+Br	n.d	22	40	10	21	74	29	220	39	n.d.
PFDA	n.d	7,3	6,3	27	100	62	150	82	120	n.d.
PFUdA	3,2	15	24	120	60	178	490	150	300	n.d.
PFDoA	n.d	4,3	8,9	15	16	25	130	130	93	n.d.
PFTrDA	n.d	12	23	130	50	100	410	460	390	n.d.
PFTeDA	n.d	n.d	3,1	6,2	6,9	13	66	150	63	n.d.
SUM ΣPFAS4	n.d	53	62	69	760	310	260	290	410	13
SUM WFD prel PFAS24	13	330	380	1500	3400	2500	5300	3600	4700	48
SUM ΣPFAS TOT	10	130	180	380	1000	818	1600	1600	1400	37
PFAS4/PFAS TOT (%)	n.d	40	34	18	74	38	16	18	29	35

PFAS (ng/kg FW)	Fish gratin	Salmon cassarole	Dill risotto	Cod and mash	Fish gratin	Meatball /potato	Pasta Bolognese
(c)	Alaska pollock	Salmon / farmed	Salmon / farmed	Cod	Cod	Beef / pork	Beef
PFBS	n.d	n.d	n.d	n.d	n.d	n.d	n.d
PFBSA	n.d	n.d	n.d	1,4	1,2	n.d	n.d
PFHpA	n.d	n.d	n.d	n.d	n.d	n.d	n.d
PFHxSA Lin+Br	n.d	n.d	n.d	2,7	1,6	n.d	n.d
PFHxS Lin+Br	n.d	n.d	n.d	n.d	n.d	2,0	n.d
PFOA Lin+Br	n.d	n.d	n.d	n.d	n.d	n.d	n.d
6:2 FTS	n.d	n.d	n.d	n.d	n.d	n.d	n.d
8:2 FTS	n.d	n.d	n.d	n.d	n.d	n.d	n.d
PFHpS	n.d	n.d	n.d	n.d	n.d	n.d	n.d
PFECHS	n.d	n.d	n.d	n.d	n.d	n.d	n.d
PFNA	4,5	n.d	n.d	5,4	6,2	n.d	n.d
PFOS Lin+Br	n.d	n.d	n.d	5,2	3,2	11	n.d
PFOSA Lin+Br	n.d	n.d	n.d	27	22	n.d	n.d
PFDA	5,8	n.d	n.d	7,5	6,3	n.d	n.d
PFUdA	11	3,7	3,2	18	13	n.d	n.d
PFDoA	n.d	n.d	n.d	3,0	4,3	n.d	n.d
PFTrDA	3,0	n.d	n.d	6,7	5,6	n.d	n.d
PFTeDA	n.d	n.d	n.d	n.d	n.d	n.d	n.d
SUM PFAS4	4,5	n.d	n.d	33	29	13	n.d
SUM WFD prel PFAS24	135	15	13	208	189	23	n.d
SUM PFAS TOT	24	3,7	3,2	77	64	13	n.d
PFAS4/PFAS TOT (%)	19	n.d	n.d	43	45	100	n.d

= PFBS + precursor
= PFHxS + precursor
= PFOS + precursor
= PFOA + precursor
= PFNA

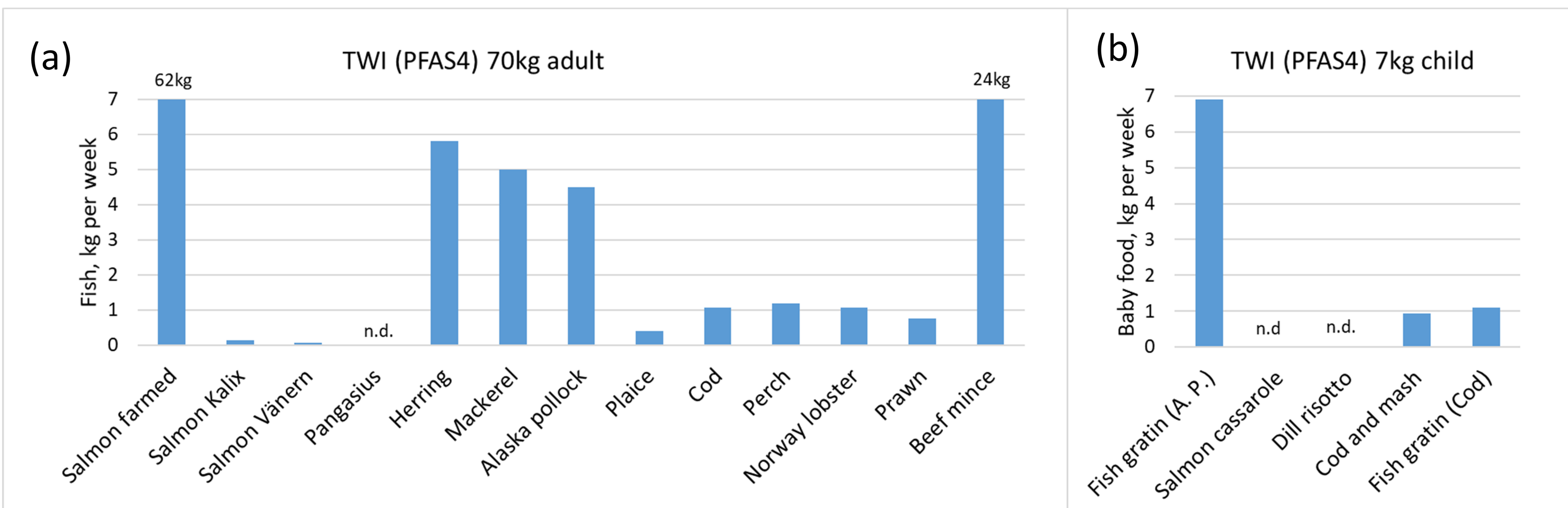

Fig 1. Calculated weekly intake in kg to reach TWI **(a)** Fish, 70kg BW (adult), **(b)** Babyfood, 7kg BW (child). n.d. denotes no detected PFAS

The five cod samples displayed a similar profile and total levels varied within a factor of two. The same applied to the farmed salmon and perch. The fraction of PFAS4 of total PFAS for the fish products was 39±23% (mean±s.d.). Br forms, when above LOQ, equalled for PFHxSA 16±11%, PFOSA 10±5% and PFOS 5±3%. For PFHxS and PFCA no detectable Br could be found. For perch, liver was also analysed and a similar profile was found but on average 6.8 times higher.

Calculations of weekly amounts equalling the TWI value were made (Fig 1). For fish a body weight of 70kg was assumed and for baby food 7kg. There was a notable difference for farmed vs wild salmon (62 vs ~0.1 kg). The cod based baby food would correspond to about 5 jars. The foods were made with 9-11% fish and on average the samples contained 9.5±4.1% of the corresponding fish, suggesting good agreement and few other sources.

Discussion

The results demonstrate the ubiquitous prescence of PFAS in fish for consumption. The basic pattern of wild fish with PFOS being the major PFAS and significant levels of in particular odd number long PFCA has been seen in other studies (e.g. TemaNord, 2019; Valsecchi et al, 2021). The results are comparable to those seen purchased fish from Scandinavia (Sadia et al, 2020; Hlouskova et al., 2013) or caught at Faroe Islands (Eriksson et al, 2013). Regarding the wild salmon it is more comparable to monitoring levels in the Bothnian Sea (e.g. TemaNord, 2019). With respect to the fractions of br-PFOS/PFHxS they can be compared to the ranges <1-22% and <20% in TemaNord (2019). The finding of Chu et al (2016) of frequent detection of PFBSA without PFBS being present is confirmed here. Also PFHxSA seems to be more common than PFHxS. Moreover, the importance of PFOSA is observed. In the Tyrifjorden case (NGI, 2019) a significant share of PFOSA occurred alongside PFOS in many liver/muscle samples. PFOSA/ PFHxSA are precursors that may degrade to PFOS/ PFHxS and thus contribute to PFAS4. The highest concentrations of PFOA were found for crustaceans, a finding seen for other species determined as well (not shown).

The EU limit values vary for the fish and meat studied (PFAS4: 1.3-45 µg/kg), but the specific limit for baby food production (2 µg/kg) is exceeded by the wild salmon. PFAS4 did not reflect the composition of e.g. long PFCA in most samples. Weighted WFD PFAS24 ranged between 10-17500 ng/kg PFOA eqv. Though not regulatory applicable to most samples, a comparison to the proposed EQS of 77 suggested no wild fish or baby food made with it, would meet this value. The perch had among the largest PFAS24 despite the remote location of the lake. Sums are comparble to those observed for perch and herring in the Baltic sea (NRM, 2023).

Conclusions

- 42 PFAS were determined in purchased fish, wild caught perch and baby food. 16 were identified.
- PFOS was typically the major PFAS observed. C9-C14 PFCA were also observed at high concentrations
- Branched PFOS, and sulphonamides 5-14% were found, stressing br-forms should be considered
- The novel sulphonamides PFBSA and PFHxSA were found in most samples, but not PFBS. PFOSA was frequently relevant compared to PFOS.
- Highest total PFAS found for wild salmon, lowest for farmed fish (salmon/pangasius)
- PFAS4 followed the order PFOS > PFNA > PFHxS > PFOA with some exceptions
- PFAS4 of total PFAS ranged from 7-100% (ave 39%), indicating that more PFAS should be examined
- Precursors such as PFHxSA and PFOSA could possibly make significant contributions to PFAS4.
- Possible weekly intake to reach TWI varied between 0.1-62kg (adult) and ~1kg cod based baby food (child)
- The EU limit (2 µg/kg FW) for PFAS4 for baby food production was exceeded for wild salmon
- All wild fish and baby food based on it showed weighted PFAS24 beyond the proposed WFD EQS (77 ng/kg PFOA eqv). This needs to be assessed in relation to monitoring and contaminated sites

References
Chu, S., Letcher, R.J., McGoldrick, D.J., Backus, S. M. Environ. Sci. Technol. 2016, 50, 669
Eriksson, U., Kärrman, A., Rotander, A., Mikkelsen, B., Dam, M. Environ Sci Pollut. Res. 2013, 20, 794
Hlouskova, V. et al., Food Additives Contam Part A, 2013, 30, 1918
NGI. 2019. PFAS Tyrifjorden 2018. report: 20180256-01-R, Oslo
NRM. 2023. Report 6:2023. Swedish Museum of Natural History, Stockholm
Sadia, M., Yeung, L.W.Y., Fiedler, H. Env Pollut, 2020, 263A, 113721
Valsecchi, S. et al. Environ Toxicol. Chem. 2021, 40, 658

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