TISSUE DISTRIBUTION OF POLYFLUORINATED COMPOUNDS FROM COMMON SEALS (*PHOCA VITULINA*) IN THE NORTH SEA

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Introduction

Recently polyfluorinated compounds (PFCs) were discovered as new emerging persistent organic pollutants. PFCs are widely used in lots of consumer products such as polymerization aids, stain repellents on carpets, textiles, leather, and paper products over the past 50 years. Scientific concern about PFCs increased due to their global distribution and ubiquitous detection in the environment, especially in marine mammals ¹. PFCs bind to blood proteins instead of fatty tissue ². The longer chained PFCs are known to bioaccumulate ³ and toxic effects in biota like neuroendocrine effects ⁴ and peroxisome proliferation ⁵ were examined. In addition positive correlation between diet of infection diseases of river otters and high concentration of PFCs was observed ⁶. For the whole body burdens are often use liver tissue and plasma, these estimation are often faulty because little is known about the distribution of PFCs in the body. The aim of this study is the determination of the distribution of PFCs in tissue of Common Seals (*Phoca vitulina*) from the North Sea.

Materials and Methods

In this study 40 PFCs were determined from the following groups: one fluorotelomer sulfonate, seven perfluorosulfonates (PFSAs), three perfluorosulfinates (PFSiAs), sixteen perfluorocarboxylic acids (PFCAs), three fluorotelomer acids, three unsaturated telomer acids, four perfluorosulfonamides (FOSAs) and three perfluorosulfonamidoethanols (FOSEs). In addition 20 mass-labelled standards were used as internal standards (IS). For the whole body burdens the samples from brain, thymus, thyroid, muscle, whole blood, blubber, liver, lung, kidney and heart were examined from four Common Seals (*Phoca vitulina*) from the North Sea. All tissue samples were homogenised using an Ultraturrax (supplied from IKA) with plastic dispersing. Approximately 2 g tissue and 2 mL blood samples were weighed in polypropylene tubes for the extraction, respectively. The tissues were extracted with acetonitrile three times for 30 min. For the clean-up of the samples Supelclean ENVI-Carb SPE cartridge (supplied from Supelco) were used. All extracts were analysed using high performance liquid chromatography-negative electrospray ionisation-tandem mass spectrometry (HPLC-(-)ESI-MS/MS).

Results and Discussion

18 of 40 target analytes were found in all tissue samples (i.e. C₄ to C₁₀ PFSAs, perfluorooctanesulfinate (PFOSi), C₈ to C₁₅ PFCAs, Perfluorosulfonamide (PFOSA) and n-methylperfluorobutane sulfonamidoethanol (MeFBSE)) (see Table 1). The dominated compound in the tissues was perfluorooctanesulfonate (PFOS) on average over 90 % relating to the other detected PFCs. The composition of perfluorohexanesulfonate (PFHxS), perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA) was low with 2.7, 1.7 and 1.5 %, respectively and for the other PFCs under 1 %. The highest PFCs sum concentrations were detected in the liver (1029 ng g^{-1} wet weight (w.w.)), lung (462 ng g^{-1} w.w.) and blood (381 ng g^{-1} w.w.). The calculation of the whole body burdens distribution based on the individual tissue masses of the whole organs (concentration in the sub-sample x tissue weight). The organs from thymus, thyroid, liver, kidney and heart were tarred directly. The content of the blood, brain, lung and muscle was calculated based on the mass information found in the literature ⁷⁻⁹. The blubber content was estimated with the dorsal blubber thickness, standard length and body mass as described by Ryg et al. ¹⁰. The whole body burdens were related as follows: blood = liver > muscle > lung > blubber > Heart > kidney > brain >> thymus >> thyroid (see Figure 1). The whole body burden of PFCs was estimated with 2.6 ± 1.3 mg absolute (n = 4, Common Seals). In the calculation was included all the examined tissue, which was around three-fourths of the whole body weight. Among others the skeleton and the pelt was unaccounted for the calculation because of the difficult extraction of them and expected low PFC concentration. In most studies PFOS was the dominated PFC in marine animals^{3, 11}. PFCAs were detected in seal liver in the Canadian Arctic in the same range as in this study, except of PFOS, which was found on one magnitude lower¹²,

¹³. The tendency of increasing PFOS concentration was comparable to this study in Harbor Seal (*Phoca vitulina*) (kidney > liver > blubber) ¹¹, Ringed Seal (*Phoca hispida*) (liver > lung > heart and liver > spleen > kidney, respectively) ¹³ and Rainbow Trout (*Oncorhynchus mykiss*) (blood > kidney > liver) ¹⁴. The study provides advice on the analysis of the whole body burdens in Common Seals for individual PFCs. This is relevant for calculation of the bioaccumulation potential of these compounds in marine mammals.

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References

1. Giesy J. P. and Kannan K. Environ. Sci. Technol. 2001; 35: 1339.

2. Jones P. D., Hu W. Y., De Coen W., Newsted J. L. and Giesy J. P. Environ. Toxicol. Chem. 2003; 22: 2639.

3. Martin J. W., Smithwick M. M., Braune B. M., Hoekstra P. F., Muir D. C. G. and Mabury S. A. *Environ. Sci. Technol.* 2004; 38: 373.

4. Austin M. E., Kasturi B. S., Barber M., Kannan K., Mohan Kumar P. S. and Mohan Kumar S. M. J. *Environ. Health Perspect.* 2003; 111: 1485.

5. Goecke-Flora C. M. and Reo N. V. Chem. Res. Toxicol. 1996; 9: 689.

6. Kannan K., Perrotta E. and Thomas N. J. Environ. Sci. Technol. 2006; 40: 4943.

7. Bininda-Emonds O. R. P. Mar. Mamm. Sci. 2000; 16: 469.

8. Burns J. M., Costa D. P., Frost K. and Harvey J. T. Physiol. Biochem. Zool. 2005; 78: 1057.

9. Stewardson C. L., Hemsley S., Meyer M. A., Canfield P. J. and Maindonald J. H. J. Anat. 1999; 195: 235.

10. Ryg M., Lydersen C. and Markussen N. H. Can. J. Fish. Aquat. Sci. 1990; 47: 1223.

11. van de Vijver K., Hoff P., Das K., Brasseur S., van Dongen W., Esmans E., Reijnders P., Blust R. and de Coen W. *Environ. Sci. Technol.* 2005; 39: 6978.

12. Butt C., Muir D. C., Stirling I., Kwan M. and Mabury S. A. Environ. Sci. Technol. 2007; 41: 42.

13. Sturman S., Small J., Solomon K. R. and Muir D. C. SETAC Europe Annual Meeting 2007.

14. Martin J. W., Mabury S. A., Solomon K. R. and Muir D. C. G. Environ. Toxicol. Chem. 2003; 22: 196.

	liver	kidney	lung	heart	blood	brain	muscle	thyroid	thymus	blubber
PFBS	$\begin{array}{c} 0.32 \pm \\ 0.34 \end{array}$	$\begin{array}{c} 0.10 \pm \\ 0.15 \end{array}$	0.17 ± 0.16	0.13 ± 0.18	4.32 ± 8.45	n.d.	$\begin{array}{c} 0.024 \pm \\ 0.049 \end{array}$	0.11 ± 0.22	$\begin{array}{c} 0.068 \pm \\ 0.12 \end{array}$	n.d.
PFPS	1.75 ± 2.46	0.085 ± 0.11	$\begin{array}{c} 0.086 \pm \\ 0.051 \end{array}$	$\begin{array}{c} 0.043 \pm \\ 0.07 \end{array}$	5.90 ± 11.66	n.d.	n.d.	n.d.	0.068 ± 0.060	n.d.
PFHxS	6.90 ± 4.03	5.68 ± 3.83	8.14 ± 4.82	4.32 ± 3.33	3.16 ± 1.08	1.58 ± 1.00	1.94 ± 1.41	4.11 ± 2.64	10.49 ± 6.19	$\begin{array}{c} 0.66 \pm \\ 0.48 \end{array}$
PFHpS	2.27 ± 2.29	1.24 ± 0.87	3.67 ± 2.67	1.32 ± 1.15	$\begin{array}{c} 0.66 \pm \\ 0.66 \end{array}$	$\begin{array}{c} 0.66 \pm \\ 0.45 \end{array}$	0.41 ± 0.32	1.22 ± 1.17	3.43 ± 2.51	0.10 ± 0.15
PFOS	1017 ± 536	288 ± 117	433 ± 227	143 ± 40	349 ± 370		59 ± 52		312 ± 136	8 01 +
PFNS	0.74 ± 0.74	$\begin{array}{c} 0.061 \pm \\ 0.086 \end{array}$	0.11 ± 0.12	n.d.	$\begin{array}{c} 0.10 \pm \\ 0.11 \end{array}$	n.d.	n.d.	0.075 ± 0.15	0.11 ± 0.040	n.d.
PFDS	$\begin{array}{c} 0.53 \pm \\ 0.38 \end{array}$	0.14 ± 0.16	$\begin{array}{c} 0.18 \pm \\ 0.16 \end{array}$	$\begin{array}{c} 0.060 \pm \\ 0.075 \end{array}$	0.12 ± 0.13	0.039 ± 0.078	n.d.	0.12 ± 0.15	$\begin{array}{c} 0.20 \pm \\ 0.084 \end{array}$	$\begin{array}{c} 0.026 \pm \\ 0.030 \end{array}$
PFOSi	$\begin{array}{c} 0.049 \pm \\ 0.077 \end{array}$	n.d.	$\begin{array}{c} 0.017 \pm \\ 0.035 \end{array}$	n.d.	0.027 ± 0.045	n.d.	n.d.	n.d.	n.d.	n.d.
Σ PFSAs/PFSiAs	1030	295	445	149	364	101	61.4	67.4	327	9.70
PFOA	0.70 ± 0.59	0.40 ± 0.41	0.75 ± 0.46	$\begin{array}{c} 0.42 \pm \\ 0.42 \end{array}$	$\begin{array}{c} 0.62 \pm \\ 0.58 \end{array}$	$\begin{array}{c} 0.057 \pm \\ 0.10 \end{array}$	$\begin{array}{c} 0.074 \pm \\ 0.11 \end{array}$	0.093 ± 0.11	$\begin{array}{c} 0.70 \pm \\ 0.25 \end{array}$	0.025 ± 0.038
PFNA	15.3 ± 5.75	3.64 ± 0.62	$\begin{array}{r} 4.84 \pm \\ 2.06 \end{array}$	$\begin{array}{c} 2.07 \pm \\ 0.84 \end{array}$	3.93 ± 2.08	$\begin{array}{c} 1.20 \pm \\ 0.50 \end{array}$	0.96 ± 0.35	1.90 ± 1.19	4.99 ± 1.22	0.61 ± 0.27
PFDA	15.2 ± 4.49	4.11 ± 2.09	5.18 ± 1.63	2.44 ± 1.06	4.38 ± 2.35	1.55 ± 0.47	1.09 ± 0.46	1.23 ± 0.59	5.65 ± 2.04	0.29 ± 0.22
PFUnDA	5.26 ± 1.59	1.92 ± 0.69	$\begin{array}{c} 2.80 \pm \\ 0.88 \end{array}$	$\begin{array}{c} 1.36 \pm \\ 0.50 \end{array}$	1.71 ± 0.84	1.06 ± 0.16	0.26 ± 0.16	$\begin{array}{c} 0.31 \pm \\ 0.34 \end{array}$	$\begin{array}{c} 2.30 \pm \\ 0.57 \end{array}$	$\begin{array}{c} 0.088 \pm \\ 0.10 \end{array}$
PFDoDA	1.47 ± 0.49	0.75 ± 0.37	1.10 ± 0.43	0.54 ± 0.25	0.47 ± 0.24	0.51 ± 0.36	0.06 ± 0.11	$\begin{array}{c} 0.18 \pm \\ 0.35 \end{array}$	0.42 ± 0.13	0.042 ± 0.067
PFTriDA	1.53 ± 0.55	1.01 ± 0.54	1.27 ± 0.63	0.77 ± 0.47	0.76 ± 0.34	0.73 ± 0.55	0.12 ± 0.83	0.51 ± 0.43	$\begin{array}{c} 1.00 \pm \\ 0.16 \end{array}$	0.12 ± 0.090
PFTeDA	$\begin{array}{c} 0.22 \pm \\ 0.16 \end{array}$	$\begin{array}{c} 0.051 \pm \\ 0.059 \end{array}$	0.16 ± 0.22	$\begin{array}{c} 0.058 \pm \\ 0.12 \end{array}$	0.076 ± 0.064	0.10 ± 0.12	n.d.	$\begin{array}{c} 0.049 \pm \\ 0.069 \end{array}$	0.21 ± 0.17	n.d.
PFPeDA	n.d.	n.d.	$\begin{array}{c} 0.13 \pm \\ 0.26 \end{array}$	n.d.	0.036 ± 0.051	n.d.	n.d.	n.d.	n.d.	n.d.
Σ PFCAs	39.7	11.9	16.2	7.65	12.0	5.20	2.55	4.27	15.3	1.17
PFOSA	1.55 ± 0.69	0.62 ± 0.44	$\begin{array}{c} 0.40 \pm \\ 0.027 \end{array}$	$\begin{array}{c} 0.27 \pm \\ 0.18 \end{array}$	5.06 ± 1.23	0.14 ± 0.14	$\begin{array}{c} 0.067 \pm \\ 0.079 \end{array}$	0.019 ± 0.024	$\begin{array}{c} 0.46 \pm \\ 0.38 \end{array}$	0.027 ± 0.038
MeFBSE	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.14 ± 0.27	n.d.	0.50 ± 1.00
Σ FOSAs/FOSEs	1.55	0.62	0.40	0.27	5.06	0.14	0.07	0.16	0.46	0.53
Σ PFCs	1071	308	462	157	381	106	64.0	71.8	343	11.4

Table 1: PFC concentration (ng g⁻¹ wet weight \pm SD) for different tissues of Common Seals (*Phoca vitulina*) from the North Sea (n = 4).

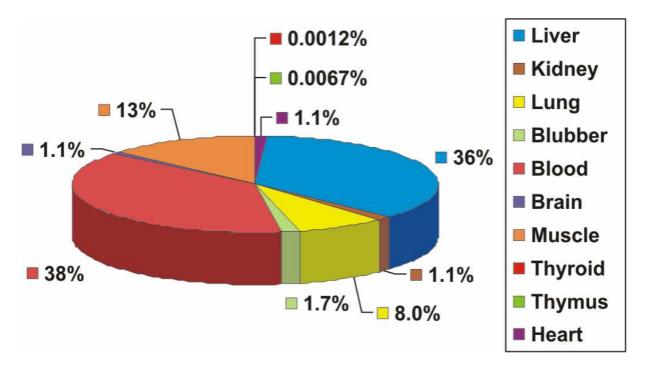


Figure 1: PFC whole body burden distribution for Common Seals (*Phoca vitulina*) from the North Sea (n = 4).