RETROSPECTIVE MONITORING OF PERFLUORINATED COMPOUNDS IN FISH FROM GERMAN RIVERS AND COASTAL MARINE ECOSYSTEMS

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Introduction

Because of their unique surface-active properties, perfluorinated compounds (PFCs) with an acidic end group have been used in a wide variety of industrial and consumer applications (e. g. galvanic, photographic, paper and textile industries) since the 1950s. Due to their very strong C-F bonds, PFCs are resistant to chemical, microbial or photochemical degradation and are consequently ubiquitously distributed in the environment [1]. As PFCs with long carbon chains like perfluorooctane sulfonate (PFOS) in addition are toxic and have a high potential to bioaccumulate [2], the production and use of C_8-based PFCs has been restricted on a voluntary and regulatory basis since 2002 [3]. Since then, it has been highly interesting to observe possible changes of environmental PFC burdens.

In this study, we report on time trends of PFCs in major German rivers in comparison with some remote areas (one enclosed lake and marine coastal areas). The investigations were carried out by retrospective monitoring of fish tissues from the years 1995 to 2010 archived by the German Environmental Specimen Bank (ESB). Concentrations of 10 perfluorinated carboxylates (PFCAs), 5 perfluorinated sulphonates (PFSAs), and 1 perfluorinated sulfonic acid amide (PFOSA) in muscle and liver tissue of bream (*Abramis brama*) and eelpout (*Zoarces viviparus*) were investigated.

Materials and methods

Bream and eelpout were sampled and processed following ESB standard operations [4, 5]. Pooled samples of liver or muscle tissue from twenty individual breams (aged 8 to 12 years) and up to 250 individual eelpouts (aged 1 to 4 years), respectively, were used for extraction. 2 g of muscle tissue and 1 g of liver tissue, respectively, were extracted with acetonitrile. Before extraction, several ^{13}C labeled PFCAs, one ^{13}C and one ^{18}O labeled PFSA, and one ^{13}C labeled perfluorinated sulphonic acid amide were added as internal standards. The extracted fat was separated by freezing, and the volume of the extract was reduced to 1 mL. PFCAs ($C_5 - C_{14}$), PFSAs (C_4, $C_6 - C_8$ and C_{10}), and PFOS-2 (total of the branched isomers), as well as PFOSA (linear) and PFOSA-2 (total of the branched isomers) were analysed by liquid chromatography coupled with a triple-quad mass spectrometer (LC-MS-MS) [6]. For validation of the method, limits of quantification (LOQ), blank values, recoveries, precision of the method and linearity of the calibration were determined for each compound.

Results and discussion:

General Features

The concentration patterns of the samples exhibit some general features visualised in Fig. 1, which shows typical concentration ranges [ng/g wet weight (ww)] of the different PFCs in muscle tissue (1995-2010), liver tissue (1996-2008), and the ratio of liver/muscle for bream from the sampling site Rhine/Bimmen. PFOS was found to have by far the highest concentration in all samples (20 to 60 ng/g in muscle; 200 to 400 ng/g in liver). Concentrations of all other PFCs were more than 10 times lower. Levels of C_{10} to C_{14} perfluorinated carboxylates were in the range of 0.3 to 1.1 ng/g (muscle) and 2 to 5 ng/g (liver). The neutral PFOSA was slightly above these concentrations. PFCAs with less than 9 and PFSAs with less than 7 C atoms were close to or below the LOQ (< 0.05 to < 0.2 ng/g in muscle and < 0.1 to < 0.4 ng/g in liver, respectively).

Concentrations in liver were generally 2 to 10 times higher than in muscle, with some remarkable compound specific differences (Fig. 1).

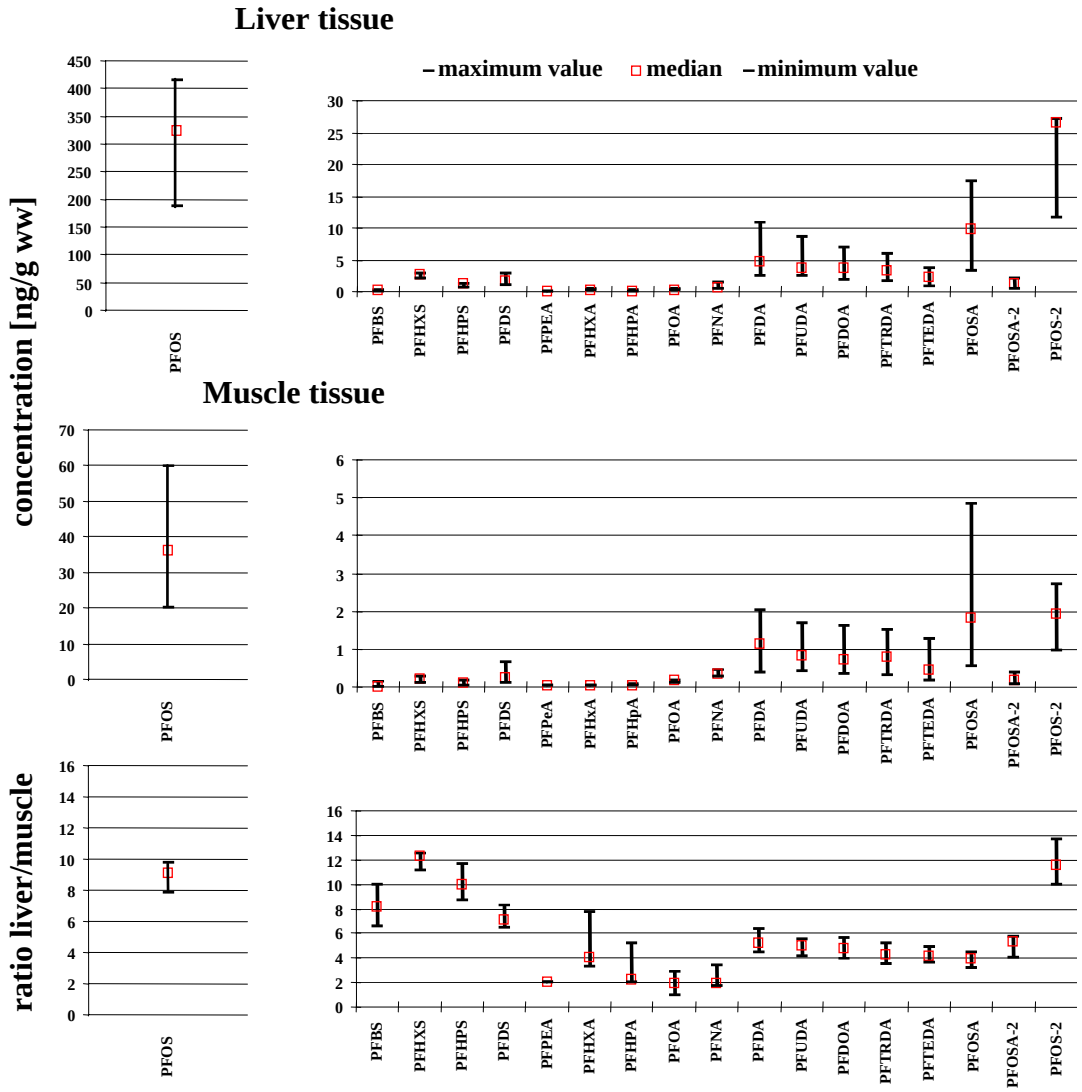

Figure 1. Typical concentrations [ng/g ww] of PFCAs (C_5 – C_{14}), PFSAs (C_4, C_6 – C_8 and C_{10}), PFOS-2 (total of the branched isomers), and PFOSA (linear) and PFOSA-2 (total of the branched isomers). Shown are mean and range concentrations of muscle tissue (1995 – 2010), liver tissue (1996 – 2008), and the liver/muscle ratio for bream from the sampling site Rhine/Bimmen.

Spatial distribution and temporal trends

Specific differences in PFC concentrations of the various sampling sites and their temporal trends in the time period from 1995 to 2010 are shown in Figs. 2 and 3 for PFOS and PFDA, respectively. These two compounds show clear differences in their temporal development. The temporal trends of the other PFCs resemble either one of these two general trends. The PFOSA temporal trend mostly resembled that of PFOS, while the longer-chain carboxylates (C-chain > 10) behaved like PFDA.

PFOS showed clearly decreasing concentration trends at most stations. At a few stations, this trend started as early as 1997 (e.g. Elbe stations E1, E2), but at most stations the downward trend started between 2000 and 2005, following a maximum.

In contrast to this, most PFDA (and the other long-chain carboxylates) exhibited increasing trends over the time period from 1995 to 2010.

PFC levels in muscle tissue showed the same trends as in liver samples.
Although PFC concentrations are in the same range in all major rivers, there are some characteristic differences deserving detailed analysis: The highest concentrations were found in the rivers Rhine and Elbe. Lower levels were observed in the Danube, and still lower levels in the river Saale.

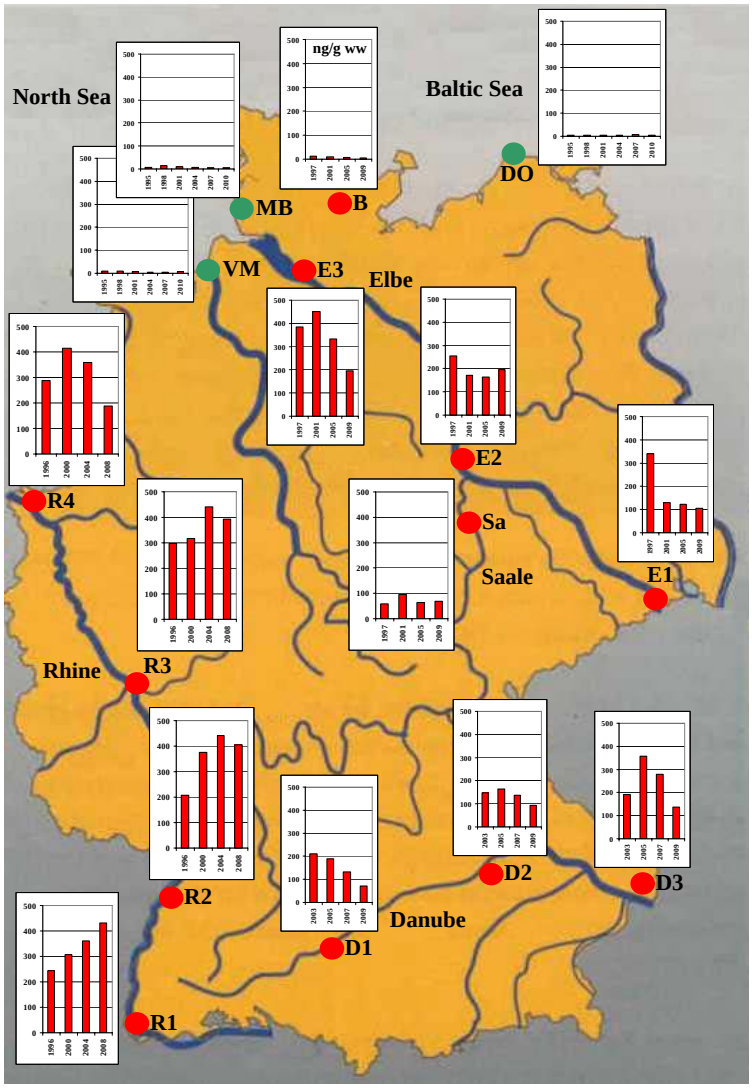

Figure 2. Trends of PFOS concentrations [ng/g ww] in bream liver from sampling sites: River Elbe: E1-Prossen, E2-Barby, E3-Blankenese; River Saale: Sa-Wettin; River Rhine: R1-Weil, R2-Iffezheim, R3-Koblenz, R4-Bimmen; River Danube: D1-Ulm, D2-Kelheim, D3-Jochenstein; Lake Belau: B and in eelpout liver from sampling sites: Varel-Mellum: VM, Meldorf Bay: MB (both North Sea), Darßer Ort: DO (Baltic Sea).

In general, no clear increase in PFOS and PFDA concentrations from source to mouth of the rivers could be observed. Besides the ubiquitous input of PFCs, local contamination from population centres in the vicinity seemed to be important.

In fish from the reference site (Lake Belau) and from the marine coastal stations in the North and Baltic Seas PFC concentration were about two orders of magnitude below the Rhine and Elbe maxima. These low "background" concentrations could be referred to many unspecific PFC sources.

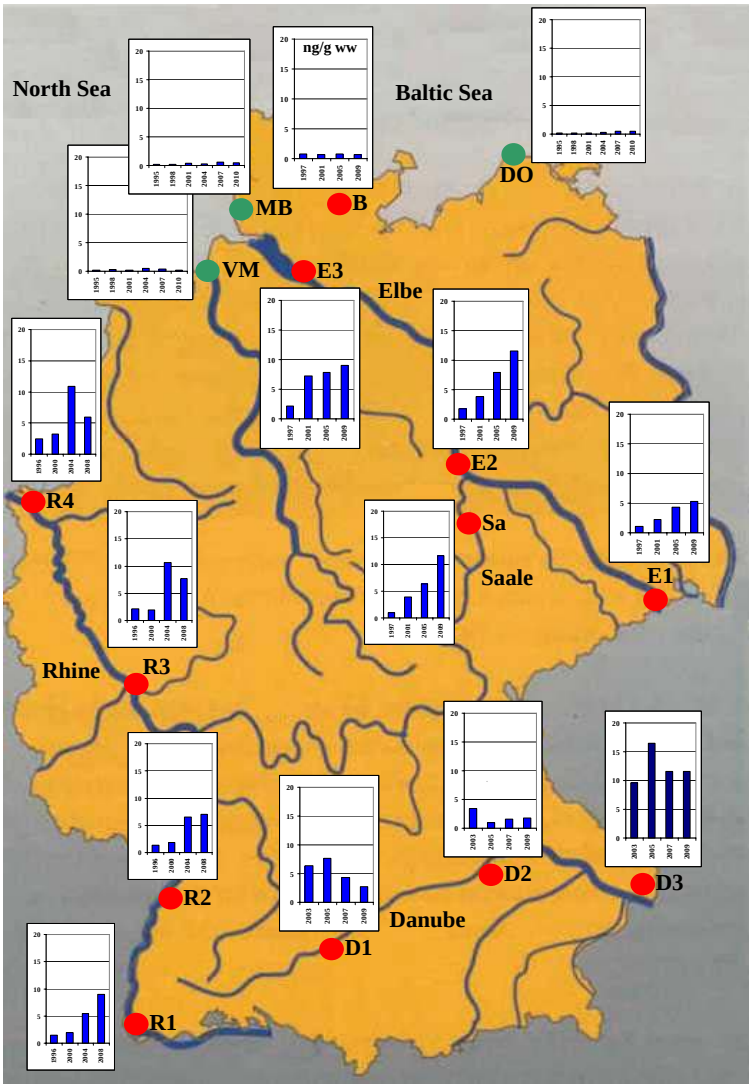

Figure 3. Trends of PFDA concentrations [ng/g ww] in bream and eelpout liver; sampling sites see Fig. 2.

Acknowledgements:
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