

Summary

The discussion on the environmental risks of perfluorinated organic pollutants mainly focuses on their persistence. Characteristic of these substances is their preferential accumulation in the liver and blood plasma instead of the fat tissue. This is the case especially for PFOS. At the beginning of the present research work very little was known about the occurrence of these substances in the marine environment. Therefore, the prevalence of PFCs in sea water, sediment and fish in the North and Baltic Sea had to be investigated with suitable methods.

The main problem was the presence of Teflon in instruments and parts of the instruments leading to high blank values. These sources for the blanks had to be found, identified and eliminated. Finally the permanent control of contamination during sampling, sample preparation and measurements is necessary.

During the practical work of the dissertation it was possible to take part in a research cruise into the Arctic. For these sea water samples with very low concentrations the method had to be optimized in order to detect and quantify such low concentrations.

Three methods for the determination of the perfluorinated sulphonic acids perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluorooctanesulfonic acid (PFOS) and the perfluorinated carboxylic acids perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNoA) and perfluorodecanoic acid (PFDeA) and perfluorooctanesulfonamide (PFOSA) in the three matrices sea water, sediment and fish (muscle and liver) were developed. All three methods were validated.

For the sea water analysis a method consisting of a solid-phase extraction and subsequent HPLC-MS-MS measurement was developed. Depending on the sea water matrix, the limits of determination of PFOA range between 0,013 and 0,03 ng/L as well as 0,007 to 0,023 ng/L for PFOS, respectively. Especially for sea water samples with low matrix content, as they are found in the Arctic, the limits of determination are partly limited by blank values (PFOA and PFNoA).

For sediment samples a method consisting of a threefold extraction with methanol and subsequent cleaning of the extracts with solid-phase resin was developed. The limit of determination for PFOA is determined by blank values and is 0,13 µg/kg dry weight. During sample preparation lower blank values had been detected and, therefore, the limits of determination were defined by the signal-to-noise ratio with a lower value of 0,05 µg/kg dry weight for PFOA. For PFOS the limit of determination is 0,05 µg/kg dry weight.

For the method development of the biota sample analyses, the clean-up procedure of the sample extracts has been very important, because, despite of extraction with methanol, the content of matrix was not negligible. The method includes a triple extraction with methanol, sequential freezing-out of lipids and matrix content and a clean-up with solid-phase material. For the HPLC-MS-MS measurement the method for the separation of the analytes by HPLC was refined and improved. The limits of determination are 0,5 µg/kg wet weight for PFOA and 0,6 µg/kg wet weight for PFOS (fish liver), respectively, 0,4 µg/kg wet weight for PFOA and 0,58 µg/kg wet weight for PFOS (fish filet) and are mainly determined by blank values.

For water samples the river Elbe was identified as a regional source of perfluorinated organic pollutants into the German Bight. Main components of the PFCs are PFOA and PFOS,

whereas the concentration of PFOA is higher than PFOS in most of the cases. At the stations Stade and Cuxhaven the concentration of perfluorooctanesulfonate (with 7,9 ng/L and 3,6 ng/L) is higher than the concentration of perfluorobutanesulfonate (with 0,6 ng/L and 1,9 ng/L). The pattern for perfluorinated organic pollutants changed especially in case of perfluorobutanesulfonic acid. At the estuary of the river Rhine (stations 11 and 12) the concentrations of perfluorobutanesulfonate (with 3,9 ng/L and 2,5 ng/L) are higher than those of perfluorooctanesulfonate (with 3,1 ng/L and 1,9 ng/L). The reason for this is an entry mainly of perfluorobutanesulfonate caused by the river Rhine. The highest concentrations of PFOS with a concentration of 7,9 ng/L and PFOA with a concentration of 9,0 ng/L are found in the river Elbe at the station Stade. The concentrations in the German Bight are below these values: PFOS was found with a concentration of 3,6 ng/L at station Cuxhaven respectively with 0,08 ng/L in the outer German Bight (station NSGR 2), PFOA was quantified with a concentration of 5,3 ng/L at the station Cuxhaven and 0,13 ng/L in the outer German Bight (Station „Ente 3“). A clear gradient exists towards the central North Sea. In the polar sea the concentrations range between 0,03 and 0,11 ng/L for PFOA and 0,01 and 0,09 ng/L for PFOS. The highest concentrations found in the Arctic are nearby Tromsø, the lowest concentrations were determined in the central Greenland Sea. In the Baltic Sea the concentrations of PFOS and PFOA were detected between 0,47 ng/L and 1,1 ng/L for PFOA and between 0,33 ng/L and 0,9 ng/L for PFOS. The highest concentrations of PFOS and PFOA were quantified nearby the estuary of the river Oder.

PFOS and PFOA were detected most frequently in sediment samples from the North and Baltic Sea. The highest concentrations of PFOA and PFOS could be determined at the station SSL (Sylter Sand Loch), where the values were 2,43 µg/kg dry weight for PFOS and 1,58 µg/kg for PFOA. The quantified concentrations in the North Sea of PFOS ranged between 2,43 µg/kg dry weight (station SSL) and 0,038 µg/kg dry weight (station UE 67), the concentrations of PFOA were between 1,58 µg/kg dry weight and 0,079 µg/kg (station UE 67). The concentrations in sediments from the Baltic Sea ranged between 0,67 µg/kg (station Mecklenburger Bucht) and 0,061 µg/kg (station Oder). The sediments from the Baltic Sea were less contaminated than the sediments from the North Sea.

The developed method for biota samples was applied to fish samples from the North and Baltic Sea. In the liver samples the main components detected were PFOS and PFOA. The determined concentrations are a first hint that fish in North and Baltic Sea are burdened with perfluorinated organic pollutants. Furthermore, the results showed that the fish muscle samples are clearly lower contaminated as compared to the fish liver samples. Remarkable is that, in contrast to water samples, the concentration of PFOS is higher than the concentration of PFOA. This implies that there is a higher bioaccumulation of PFOS compared to PFOA.

The new developed analytical methods allow to examine PFCs in all investigated matrices (water, sediment and biota). Because most of the target analytes could be found everywhere in the North and Baltic Sea the results underline that the PFCs are a very important new pollutant group with PFOA and PFOS as main compounds.