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SPATIAL AND TEMPORAL TRENDS OF PERFLUOROALKYL SUBSTANCES IN SWEDISH HERRING

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Introduction

Perfluoroalkyl acids (PFAAs) are a group of anthropogenic surfactants consisting of a fully fluorinated, hydrophobic alkyl chain with typically 4 to 18 carbon atoms and a hydrophilic functional group (1, 2). PFAAs have been produced since the beginning of the 1950s for use in a wide range of consumer products and commercial processes. Today, PFAAs are recognized as ubiquitous environmental contaminants, owing to their global occurrence in, e.g., water (3), sediment (4), biota (5), and humans (6).
The aim of this study was to examine temporal and spatial trends of PFAAs in Baltic Sea herring (Clupea harengus) from Sweden. Herring are of particular interest because they are consumed by humans and historically they have shown high concentrations of other contaminants, e.g., dioxins and PCBs. The specific objectives were to i) investigate spatial trends in herring along the Swedish coastline; ii) determine temporal trends of PFAAs in herring; and iii) explore differences in the relative profile of PFAAs in herring from different sites.

Material and methods

Fish sampling
Herring are collected annually at 17 sites along the Swedish coastline as part of the Swedish National Monitoring Programme for Contaminants in Marine Biota (7), and then stored frozen in the Environmental Specimen Bank (ESB) at the Swedish Museum of Natural History. Sampling locations are regarded as reference sites, i.e. are far from known pollution sources and ferry routes. For investigation of spatial trends, fish from all 17 reference sites plus 'higher exposed' animals from an additional 5 sites were included. These sites were chosen based on their proximity to highly populated areas and previous investigations on water quality. For the temporal trend analyses, samples from the ESB were retrospectively analysed for PFAAs. Fish sampled between the years 1980-2014 were included. Between 1980 and 2004 one pooled sample was used and analysed every second year and after 2004 two pooled samples were analysed every year. Each pool consisted of 12 fish.

Chemical analyses
The target analytes in this study were PFBS, PFHxS, PFOS, PFDS, FOSA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, and PFPeDA. FOSA was the only PFAA-precursor included in this study and is included, for simplicity, in the generic term 'PFAAs'. Sample extraction involved sonicating tissue samples in acetonitrile, followed by clean-up with activated carbon (8). The resulting extract was analysed by ultra-performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS). Individual target analytes were quantified by isotope dilution using a 5-point calibration curve.

Statistical analyses
Temporal trends were examined by log-linear regression. Non-linearity of trends was investigated by a change-point detection method suggested by Sturludottir et al. (9). The method iteratively searches for a combination of two log-linear regression lines that explains significantly more of the total variance than explained by a single regression line for the whole study period.

Results and discussion

PFOS displayed the highest concentrations in herring liver from some of the more populated/exposed areas in Sweden. For example, herring from Lilla Värtan, located in Stockholm, contained the highest levels (56 ng/g ww; Fig. 1), while fish from Gävlebukten, home of Sweden's largest harbour, displayed

PFOS levels of 25 ng/g ww. Despite these elevated concentrations, PFOS concentrations in liver from all animals were lower than the EU target level of 9.1 ng/g ww set using muscle tissue.

The spatial patterns were highly variable among substances. However, concentrations were generally greater in the Baltic Sea compared to the west coast of Sweden, which is likely due to the high residence time of water in the Baltic (~20 years)(10). The exception was for FOSA, which exhibited the highest concentrations in animals from the Swedish west coast.

Temporally, concentrations of most PFAAs increased steadily from 1980 to 2014 (see PFOS and PFUnDA, Fig. 2), with the exception of FOSA which declined over this time period. An apparent drop in concentrations over the last two to three years was observed for some substances, but this was not statistically significant. Overall, the ongoing increase of PFOS since the phase-out of this substance in 2000 is surprising, considering that in most parts of the world, a levelling off, or decline in concentrations has been reported.

The relative PFAA profile was fairly similar among sites. However, on the Swedish west coast FOSA constituted around 55% (weight basis) of the total PFAA concentration while at most other sites this substance constituted around 10% of the total PFAA concentration (Fig. 3). PFOS accounted for around 55-60% of the total PFAA levels in the northern part of Sweden. At the more exposed sites, PFOS constituted 70-80% of the total PFAA concentration, while sumPFCAs constituted 12% of the total. Moreover, on the Swedish west coast and the southernmost part of Sweden, PFNA was found in very low concentrations compared to all other sites.

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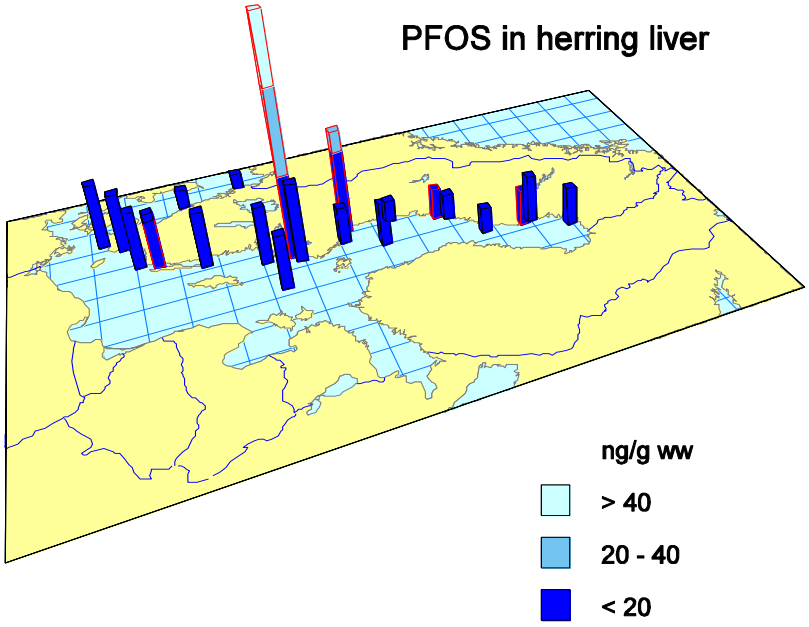

Fig. 1. PFOS concentration (ng/g ww) in herring liver along the Swedish coastline. Blue bars with a red outline represent 'higher exposed' sites (year 2011) and blue bars without the red line the reference sites (arithmetic mean of 2010-2014).

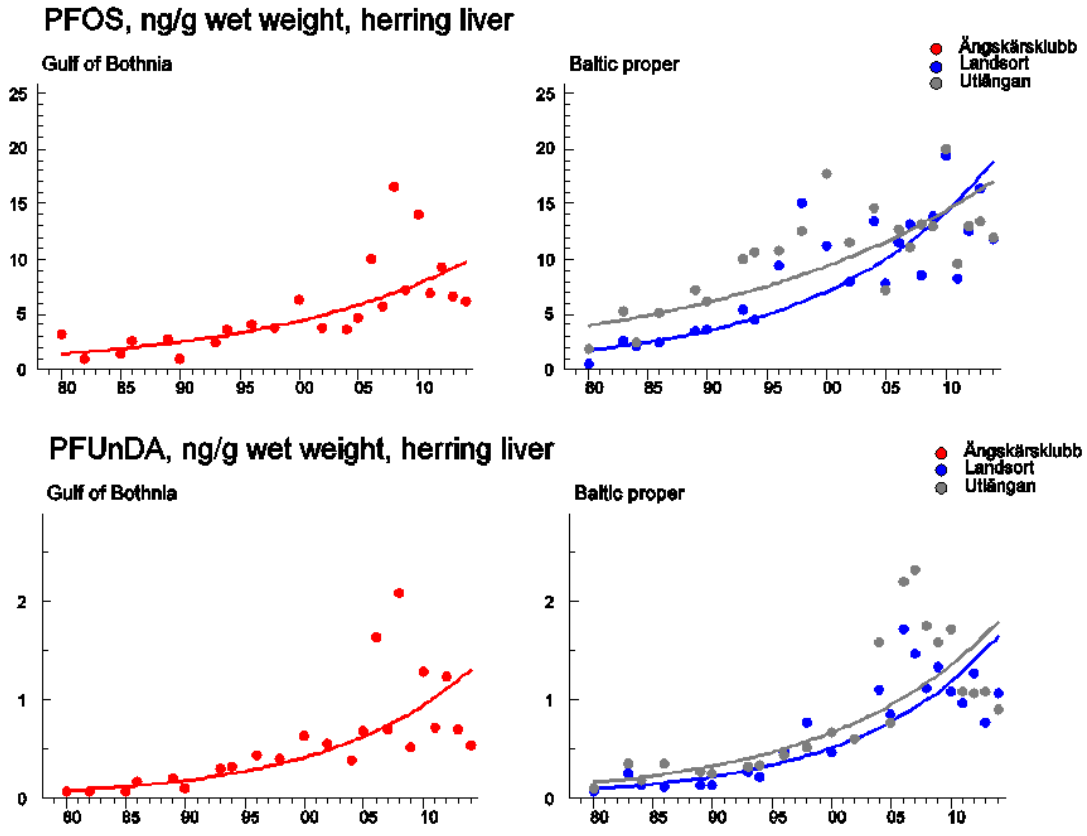

Fig. 2. Temporal trends of PFOS and PFUnDA (ng/g ww) in herring liver between 1980 and 2014 at three different sites. Each dot is the result of one pooled sample (1980-2004) or a mean of two pooled samples (2005-2014).

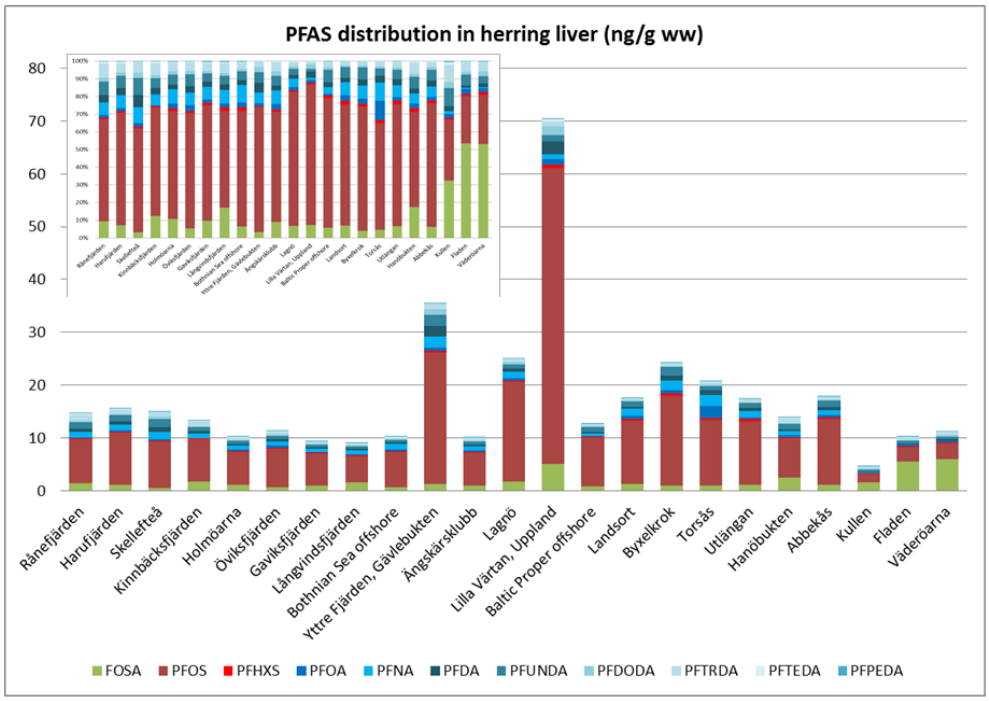

Fig. 3. Profile distribution of PFAS (ng/g ww, small picture in %). The sites going from the very north (left bars) and down in the Baltic to the west coast (right bars).