Retrospective Monitoring of Perfluorinated Compounds in Archived Herring Gull Eggs

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Abstract—Although perfluorinated compounds (PFCs) were used for many applications since the 1950s only in recent years their environmental relevance became apparent. Meanwhile the persistent, bioaccumulative and toxic potential of several PFCs has been proven. A retrospective monitoring was performed to assess concentration trends of PFCs in marine biota from the German Environmental Specimen Bank (ESB). Archived homogenate samples of herring gull (Larus argentatus) eggs covering the period 1988–2008 (North Sea; islands Trischen and Mellum) and 1991–2008 (Baltic Sea; island Heuwiese) were analyzed for a set of PFCs. Compounds detected with highest levels were perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA). North Sea eggs had higher PFOS concentrations than Baltic Sea eggs in most years. While the PFOS time series for Baltic Sea eggs showed an increasing trend, North Sea eggs revealed varying concentrations. Eggs from Heuwiese, located in a Baltic Sea region with negligible anthropogenic impacts, showed lower PFOA levels (in the range of the limit of quantification of 0.5 ng/g wet weight) than North Sea eggs. However, especially in some years quite high PFOA levels were found in gull eggs from the North Sea sites.

Keywords: Baltic Sea, biomonitoring, marine birds, North Sea, perfluorinated compounds

INTRODUCTION

Perfluorinated compounds (PFCs) are used for many applications: in the textiles industry for the impregnation of clothes, in the paper industry for the production of stain-, fat- and water resistant papers, in the photographic industry, as fire extinguishants or in the galvanic industry. PFCs detected in the environment are partly degradation products of precursor compounds while another fraction of PFCs derives from direct emissions (DeSilva and Mabury, 2006; Paul et al., 2009). Although PFCs were used for many applications since the 1950s only in recent years their environmental relevance became obvious. Increasing levels in biota mirror the increasing production of PFCs since the 1970s (Paul et al., 2009).
Meanwhile the persistent, bioaccumulative and toxic potential of several PFCs has been proven. Perfluorooctane sulfonate (PFOS), its salts and perfluorooctane sulfonyl fluoride were newly added to Annex B of the Stockholm Convention on Persistent Organic Pollutants in May 2009 (UNEP, 2009). The Stockholm Convention is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically and accumulate in humans and wildlife. It now requires Parties to take measures to eliminate or reduce the release of POPs into the environment. For compounds in Annex A production and applications are banned, for compounds in Annex B production and applications are curtailed, and for Annex C compounds a reduction of emissions is necessary.

Generally, more exposure data are required for the further risk management of PFCs by authorities. To assess the concentration trends in marine biota over the last twenty years a retrospective monitoring was performed using samples from the German Environmental Specimen Bank (ESB) (German Federal Environment Agency, 2008, 2010). The German ESB was used in recent years to provide exposure data for different groups of compounds. Examples are monitoring studies for polycyclic musk fragrances (Rüdel et al., 2006) or alkylphenolic compounds (Wenzel et al., 2004).

Since it is assumed that PFC levels are highest in the top predators of the marine food web, eggs of herring gulls were chosen as indicators in this study. Thus archived annual homogenate samples from the German ESB covering the period 1988–2008 (North Sea) and 1991–2008 (Baltic Sea) were retrieved and analyzed for a set of perfluorinated compounds including PFOS and PFOA. Sub-samples of a number of annual herring gull egg homogenates were already investigated for other compounds (e.g., metals: Rüdel et al., 2010, synthetic musk compounds: Rüdel et al., 2006; organotin compounds: Rüdel et al., 2003).

**MATERIALS AND METHODS**

Eggs of herring gulls (*Larus argentatus*) were selected as bioindicators for the German ESB according to the following criteria (German Federal Environment Agency, 2010): good availability (high abundances), stable population dynamics, reliable identification of eggs, no protection by any regulations, good understanding of the feeding habits (herring gull eggs are excellent indicators for pollution burdens in the direct vicinity of breeding colonies).

In the framework of the German ESB herring gull eggs were collected annually from the sampling sites Island Heuwiese (Baltic Sea), Island Trischen (North Sea) and Island Mellum (North Sea). Routinely, contents from about 35 eggs from each site are pooled (Paulus et al., 2003). Afterwards an annual homogenate is prepared by cryo-milling and homogenization of the material and the particle size is characterized (Koglin et al., 1997). The final homogenate is stored as sub-samples of about 10 g in glass vials in the archive of the German ESB in the gas phase above liquid nitrogen at temperatures below –150°C (Emons et al., 1997).
Sub-samples of about 90 annual egg homogenates were analyzed for this study. Seven perfluorinated carboxylic acids and five perfluorinated sulfonic acids were investigated. For most of the compounds isotopically labeled standards were available which were used as internal standards. Perfluorobutanoate (PFBA), perfluorohexanoate (PFHxA), perfluorononanoate (PFNA), perfluorooctanoate (PFOA), perfluoroundecanoate (PFUnA), perfluorododecanoate (PFDoA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS) and perfluorodecane sulfonate (PFDS) were analyzed by liquid chromatography coupled with a triple-quad mass spectrometer (LC-MS-MS). The extraction included alkaline and acidic treatments to enhance the availability of bound PFCs. The whole method was validated by standard fortification experiments at eight concentration levels (recoveries for all compounds in the range 70–120%). Data are given as ng/g wet weight (ww). Blanks were below 0.1 ng/g and limits of quantification (LOQ) were 0.5 ng/g ww for each compound. In general, samples were analyzed once. However, for determining the analytical precision, about 20 samples were analyzed in triplicate (typical standard deviations: 5–30% for PFOS and PFOA depending on the concentration level). Details are given elsewhere (Rüdel et al., 2011).

RESULTS AND DISCUSSION

Levels of the different PFCs in herring gull eggs were quite different. Figure 1 shows an overview of the detected ranges for each compound at the three sites. PFOS and PFOA showed the highest concentrations of all PFCs investigated. PFHpA, PFDA, PFUnA, PFHxS and PFHpS were detectable at significant lower concentrations, while PFNA, PFBA, PFHxA, PFBS and PFDS concentrations were below the respective LOQs in most of the samples.

Regional differences

The North Sea sampling sites designated for the ESB are located in regions
with anthropogenic impacts. The island Mellum is influenced by the estuary of
the river Weser, and the island Trischen by the estuary of the river Elbe. Input
from both rivers potentially contributes to the PFC burden of the marine organisms.
Thus, PFOA levels in eggs from the North Sea sampling sites (median values:
about 10 ng/g ww) were higher as compared to Baltic Sea eggs which stem from
a region with low anthropogenic impacts (mean value: about 1 ng/g PFOA). In
isolated years quite high levels were found for the North Sea sites (up to 120 ng/
g ww) while in most other years PFOA levels for North Sea eggs were in the range
3–20 ng/g ww. Baltic Sea herring gull eggs had PFOA levels in the range <0.5–
3 ng/g ww. In case of PFOS North Sea eggs also had higher concentrations in most
years. The median values for PFOS in herring gull eggs were about 70 ng/g ww
and 80 ng/g ww for the North Sea sites Mellum and Trischen, respectively, and
60 ng/g ww for the Baltic Sea site (Fig. 1). However, concentration differences
for PFOS between North Sea and Baltic Sea eggs diminished in recent years.
Since 2005, Baltic Sea eggs even showed higher PFOS levels as compared to eggs
from both North Sea sites.

**Temporal comparison**

PFOS concentrations in Baltic Sea eggs significantly increased from about
20 ng/g ww in 1991 to about 160 ng ww in 2008 (hatched columns in Fig. 2; 
significant positive trend: $p < 0.05$ for the non-parametric Mann-Kendall-test).
PFOS in eggs from the North Sea sites showed no temporal trend. For eggs from
Trischen high levels were found throughout the period 1994–2000 (single years
with higher PFOS values were 1988, 2002, 2008; Fig. 2) while for eggs from
Mellum higher levels were detected in 1993–1995 and 1998–2002.

**Comparison with other monitoring data from Northern Europe**

Recently several investigations on PFC levels in marine birds were reported.
For guillemot eggs from a Swedish Baltic Sea site Holmström et al. (2005) found
also significantly increasing levels of PFOS during the period 1968 to 2003 (30-
fold increase from 25 ng/g to 614 ng/g ww). However, the reported PFOS concentrations were much higher as the levels found here in Baltic Sea and even North Sea herring gull eggs, probably due to sampling from a more contaminated region or species differences in bioaccumulation potential. For herring gull eggs from Northern Norway also increasing levels of PFOS and PFOA were detected, but at a lower level (2003: PFOS about 40 ng/g ww, PFOA < 1 ng/g ww; Verreault et al., 2007).

CONCLUSIONS

The voluntary cease in production of PFOS and respective precursor substances declared by the US based primary manufacturer 3M in 2000 as well as the restricted use of PFOS in the European Union as finally announced in 2006 are not mirrored so far in continuously decreasing PFOS concentrations in wildlife. While for the North Sea ecosystem varying PFOS levels in eggs were found, Baltic Sea eggs even showed a significant increase of PFOS over the last two decades.

Higher levels of PFOA detected in the eggs as compared to other investigations are probably due to the more efficient extraction procedure which includes both an alkaline and an acidic treatment. We recommend this procedure because we assume that by this means the bioavailable amount of PFCs is better characterized (e.g., for acidic conditions during food digestion).

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