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PERFLUOROALKYL ACIDS (PFAAS) AND PRECURSORS IN BIRD EGGS FROM THE TERRESTRIAL AND FRESHWATER ENVIRONMENT

U. Eriksson[1], A. Roos[2], Y. Lind[2], A. Ekblad[1], K. Hope[1], A. Kärrman[1]

[1]*Man-Technology-Environment (MTM) Research Centre, School of Science and Technology, Örebro University, SE-70182 Örebro, Sweden*

[2]*Swedish Museum of Natural History, P.O. Box 50007, SE-104 05 Stockholm, Sweden*

Introduction

Per- and polyfluorinated alkyl substances (PFASs) is an entirely anthropogenic compound group that has been released into the environment for decades, due to their widespread use in a large number of consumer products and industrial applications, such as in paper, waxes, cleaning products, wetting agents, textiles, pesticides, aqueous fire fighting foams, and paints.[1] The PFASs manufacturing and production have put through major changes the two latest decades, primarily a switch from C8 technology towards alternatives with shorter perfluorinated alkylchain moeitys, increased fluorotelomer production, and a geographical shift with increased production in Asia.[2] These changes have to some extent been reflected in humans and environment, with decreased levels of perfluoroocatane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). Meanwhile, other PFAS homologues have increased, and newly identified and emergent compounds have got increased attention. Many of the so far studied PFAS compounds have shown to be persistent, toxic, and bioaccumulating. Therefore, raptorial birds are suitable for biomonitoring. Birds of prey are subjects to PFAS exposure through multiple exposure pathways. In the freshwater and the terrestrial environment, atmospheric transport is thought to have a major impact on PFAS contamination, in contrast to the marine environment where oceanic transportation is expected to have the major influence. The atmospheric transportation is faster than the oceanic transportation, hence this pathway provides more accurate information on recent exposure.
In this study, bird eggs from the terrestrial and the freshwater environment were analysed for a suite of PFAS, including semi-persistent precursor compounds and intermediates. There are few studies covering environmental levels of PFCA precursor compounds. Therefore, little is known about their prevalence and concentrations in wild life.
Stable isotopes can be used as a tool to elucidate the dietary trends. The $\delta^{13}C$ is generally higher in the marine environment compared to the terrestrial and freshwater environment. The $\delta^{15}N$ reflects the position in the food chain, and increases with about 2-3 ‰ for each trophic level. Since a large number of PFAS homologues are bioaccumulating, concentrations of PFASs are expected to increase with trophic level.
The objective of this study was to investigate the concentrations and patterns of PFASs in raptor birds by analysing bird eggs, to elucidate recent precursor exposure and the effects of shift in PFAS production and technology, in the terrestrial and freshwater environment.

Materials and methods

Unhatchable eggs from raptors were used in the study. Species included were osprey (Pandion haliaetus), tawny owl (Strix aluco), and common kestrel (Falco tinnunculus). Osprey is a migratory, fish-feeding species. Tawny owl is a non-migratory species, and feeds mainly on rodents. Common kestrel is a migratory species and feeds on rodents. Samples were collected from osprey in 1997 – 2001 (n=10), 2008-2009 (n=10), and 2013 (n=10), from tawny owl in 2014 (n=10), and from common kestrel in 2014 (n=40). The samples were collected in Sweden and for geographical comparison, the samples were divided into six regions; south, south-east, west, east, central, and north.
The PFAS classes included in this study were perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonic acids (PFSAs), saturated and unsaturated fluorotelomeric acids (FTCA/ FTUCAs), polyfluoroalkyl phosphate diesters (diPAPs), perfluoroalkane sulfonamides and sulfonamido ethanols (FOSA/FOSEs).
In the extraction and clean-up procedure, 0.25 g sample was used. Internal standards were added to the samples, followed by addition of 4 mL acetonitrile. The samples were shaken, for 15 min, sonicated for 15 min, and then centrifuged. The procedure was repeated once and the supernatants were combined.

Two systems were used in the analysis; one Acquity UPLC system coupled to a Quattro Premier XE mass spectrometer (Waters Corporation, Milford, USA), and one Acquity UPLC system coupled to a XEVO TQ-S triple quadrupole mass spectrometer (Waters Corporation, Milford, USA). The targeted compounds were separated on a 100 mm C18 BEH column (2.1 mm, 1.7 µm). Mobile phases used for PFCAs, PFSAs, FTCAs, FTUCAs, FOSAs, and FOSEs were water and methanol, both with 2 mM ammonium acetate. For diPAPs, water and methanol were used with addition of 2mM ammonium acetate and 5 mM 1-methylpiperidine. At least two transitions were monitored for all analytes except for PFBA and PFPeA. Stable isotopes were analysed on using an elemental analyser (model EuroEA3024; Eurovector, Milan, Italy) coupled on line to an Isoprime isotope-ratio mass spectrometer (GV-Instruments, Manchester, UK).
Labeled internal standards, and a hen egg sample spiked with native compounds included in each batch, were used to assess recoveries. The mean recoveries of labeled internal standards were in the range 68–95% for PFCAs, 91–93% for PFSAs, 56–89% for FTCAs and FTUCAs, 74% for PFOSA, 47–127% for FOSAs and FOSEs, and 135% for 6:2 FTSA. The recoveries of spiked native compounds in the hen egg were 87–107% for PFCAs, 102–129% for PFSAs, 83–102% for FTCAs and FTUCAs, 38% for PFOSA, 85-118% for FOSAs and FOSEs, 105% for 6:2 FTSA, and 89–106% for diPAPs.

Results and discussion

The bird eggs in this study were suggested by the $\delta^{13}C$ to belong solely to the freshwater and terrestrial compartments, with no influence from marine diet. The $\delta^{13}C$ for the ospreys ranged between -25.2 ‰ and -30.4 ‰, and for the common kestrels and the tawny owls between -26.2 ‰ and -30.0 ‰. Birds with elements of marine diet have a $\delta^{13}C$ >-20 ‰.[3]
Highest concentrations in the two compartments were found in the freshwater environment. PFOS was the predominating compound, with a contribution of 72% to the ∑PFAS. The concentration in the osprey egg samples from 2013 was in the range 16 – 219 ng/g, with a median value of 70 ng/g. Other abundant compounds were the long-chained PFCAs (C9 – C14), with ∑PFCA of 27.7 ng/g. Most prevalent PFCAs were perfluoroundecanoic acid (PFUnDA) (10.3 ng/g), followed by perfluorodecanoic acid (PFDA) (7.5 ng/g), and perfluorododecanoic acid (PFDoDA) (5.3 ng/g), in year 2013.
Several precursors and intermediates were detected in the freshwater environment, revealing a recent and ongoing exposure from PFASs. These semi-persistent compounds were found at lower concentrations and less frequently than other PFASs, as expected due to their fast biotic degradation rates. The quantified diPAPs were found in three eggs of osprey. Highest level of 6:2 diPAP was found in an egg from 1997 – 2001 (0.39 ng/g), and highest level of 8:2 diPAP was found in an egg from 2013 (0.95 ng/g).
The 6:2 FTSA, which both can be a degradation product from other precursor compounds and also degrade into persistent PFCAs, was found in three samples of osprey in the year 2013. The concentrations were similar to those of the persistent PFASs. Highest level of 6:2 FTSA was found in an osprey egg from 2008-2009 (52.2 ng/g).
Exposure of precursor compounds to the freshwater environment was further evidenced by detection of the intermediates FTCA/FTUCAs. 7:3 FTCA was the most frequently detected intermediates, at levels ranging between <LOD and 1.7 ng/g in osprey eggs from 2013.
In the terrestrial environment, the concentrations of PFOS and PFCAs were significantly lower, about 10-20 times lower for PFOS and five times lower for PFCAs. The PFOS median concentration was 7.9 for tawny owl, and 3.8 for common kestrel. The PFAS profile was slightly different, with higher proportion of ∑PFCA compared to the freshwater environment, 55% for common kestrel, and 41% for tawny owl, compared to 28% for osprey. PFOS though was the predominating single compound in the terrestrial environment.
Precursors and intermediates were detected in the terrestrial environment as well, in both common kestrel and tawny owl. The quantified diPAPs were found in three samples of common kestrel eggs, and 6:2 FTSA was found in one sample of tawny owl. Additionally, the intermediates FTCA/FTUCAs were found in both common kestrel and tawny owl.

Figure 1. Homologue distribution of PFAS classes in osprey eggs from 2013, common kestrel from 2014, and tawny owl from 2014.

The relatively high concentrations in the freshwater environment compared to the freshwater environment could be related to their trophic position. There were significant differences in $\delta^{15}N$ between

the freshwater and the terrestrial environment, indicating higher trophic level for the ospreys in the freshwater environment than for the tawny owls and common kestrels in the terrestrial environment. Osprey had a $\delta^{15}N$ of 13.8 ‰, while the $\delta^{15}N$ was 7.4 ‰ for tawny owl and 5.3 ‰ for common kestrel. This corresponds to a 2-3 times higher trophic level for osprey compared to tawny owl and common kestrel, since one trophic shift is represented by a shift of 2-3‰. As previously described, the levels of PFOS and long-chained PFCAs were higher in the freshwater environment compared to the terrestrial environment. It's possible that the higher levels in the freshwater environment is a result of feeding on a higher trophic level. It should be underlined that the freshwater food web is more complex than the terrestrial environment, and spans over multiple trophic levels. Another factor that could have an effect on the higher concentration in the freshwater environment compared to the terrestrial environment is the hydrophilic properties of PFASs, which make them accumulate in aquatic environments.

The semi-persistent compounds were found in all areas of Sweden. Due to low frequency of detection, geographical variations were not possible to determine for these compounds. For the persistent PFAS, geographical variances were seen, with generally higher levels in the south and the west parts of Sweden. A similar pattern was found for $\delta^{15}N$ where the levels also were higher in the south and the west parts of Sweden. The PFOS level in tawny owl was significantly higher in the south compared to the west, and in common kestrel the PFOS level was significantly higher in the south compared to the central and north parts. The variations for ∑PFCA were similar to PFOS; higher levels in the west parts compared to the east and northern parts for common kestrel and tawny owl. This suggests that it could be an association between trophic level and PFAS concentration. However, baseline values are not known, and therefore it's difficult to determine whether enhanced PFAS concentrations is a result of higher trophic level, or if other factors such as local sources, dietary habits, and precipitations is of more significant importance.

Temporal trends of PFAS concentrations where frequency of detection was above 50% were assessed for the osprey eggs over the years 1997 – 2001, 2008 – 2009, and 2013. A significant increase was found between 1997 – 2001 and 2008 – 2009 for almost all long-chained PFCAs; PFDA, PFUnDA, PFDoDA, PFTrDA, and PFTDA. Thereafter, the concentrations seem to leveling off and no significant change was observed for these compounds between 2008 – 2009 and 2013. The ∑PFCA increased from 12.4 ng/g in 1997 – 2001 to 29.5 ng/g in 2008 – 2009, and in 2013 the ∑PFCA was 27.7 ng/g.

For PFOS, the concentration remained on the same level during the whole study period, with no significant change from 103 ng/g in 1997 – 2001 to 70 ng/g in 2013. In view of the phase-out and regulations of PFOS and long-chained PFCAs, this is a poor response to the efforts made to reduce levels. For FTSAs and diPAPs, temporal trends could not be evaluated due to low frequency of recovery. However, FTSAs and diPAPs were detected not only recently, but also in the years 1997 – 2001 and 2008 – 2009, suggesting a long-term ongoing exposure from these precursor compounds.

For the bird eggs in the terrestrial environment, no temporal trends were assessed in this study. However, the mean concentration of PFOS in tawny owl eggs from 2014 in this study (14 ng/g) was higher compared to a previous study of tawny owl in Norway, where the mean level was 5.6 ng/g in 2009.[4] This suggest that response to changes in PFAS manufacturing is slow also in the terrestrial environment.

The continued high levels of PFOS, long-chained PFCAs, and the presence of precursor compounds in the bird eggs is of great concern since this pose a threat to already vulnerable species.

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References

1. Lindstrom, A.B., Strynar, M. J., and Libelo, E. L., 2011. Polyfluorinated compounds: past, present, and future. Environ. Sci. Technol. 45 (19), 7954–7961.

2. Wang, Z.Y., Cousins, I. T., Scheringer, M., Buck, R. C., and Hungerbuhler, K., 2014. Global emission inventories for C4-C14 perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, PartI:production and emissions from quantifiable sources. Environ.Int. 70, 62–75.

3. Hobson, K. A., 1987. Use of stable-carbon isotope analysis to estimate marine and terrestrial protein content in gull diets. Can. J .ZOOl. 65: 1210-1213.
4. Ahrens, L., Herzke, D., Huber, S., Bustnes, J. O., Bangjord, and J., Ebinghaus, R., 2011. Temporal trends and pattern of polyfluoroalkyl compounds in tawnyowl (Strix aluco) eggs from Norway, 1986–2009. Environ.Sci.Technol. 45 (19), 8090–8097.