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Comparison of PFASs contamination in the freshwater and terrestrial environments by analysis of eggs from osprey (*Pandion haliaetus*), tawny owl (*Strix aluco*), and common kestrel (*Falco tinnunculus*)

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ABSTRACT

The level of PFAS (per- and polyfluorinated alkyl substances) contamination in freshwater and terrestrial Swedish environments in 2013/2014 was assessed by analyzing a range of perfluorinated alkyl acids, fluorotelomer acids, sulfonamides, sulfonamidoethanols and polyfluoroalkyl phosphate diesters (diPAPs) in predator bird eggs. Stable isotopes (¹³C and ¹⁵N) were analyzed to elucidate the dietary source. The tawny owl (*Strix aluco*, n=10) and common kestrel (*Falco tinnunculus*, n=40), two terrestrial species, and the osprey (*Pandion haliaetus*, n=30), a freshwater species were included. In addition, a temporal trend (1997–2001, 2008–2009, 2013) in osprey was studied as well. The PFAS profile was dominated by perfluorooctane sulfonic acid (PFOS) in eggs from osprey and tawny owl, while for common kestrel perfluorinated carboxylic acids (Σ PFCA) exceeded the level of PFOS. PFOS concentration in osprey eggs remained at the same level between 1997 and 2001 and 2013. For the long-chained PFCAs, there were a significant increase in concentrations in osprey eggs between 1997 and 2001 and 2008–2009. The levels of PFOS and PFCAs were about 10 and five times higher, respectively, in osprey compared to tawny owl and common kestrel. Evidence of direct exposure from PFCA precursor compounds to birds in both freshwater and terrestrial environment was observed. Low levels of diPAPs were detected in a few samples of osprey (< 0.02–2.4 ng/g) and common kestrel (< 0.02–0.16 ng/g) eggs, and 6:2 FTSA was detected in a majority of the osprey eggs (< 6.3–52 ng/g). One saturated telomer acid (7:3 FTCA), which is a transformation marker from precursor exposure, was detected in all species (< 0.24–2.7 ng/g). The ¹⁵N data showed higher levels in osprey eggs compared to tawny owl and common kestrel, indicating that they feed on a 2–3 times higher trophic level. We conclude that ospreys are continuously exposed to PFAS at levels where adverse toxic effects have been observed in birds.

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1. Introduction

Per- and polyfluorinated alkyl substances (PFASs) are widely used in a large range of industrial and consumer products, despite increasing awareness and knowledge amongst scientists and policy makers about their environmental impact and fate (Buck et al., 2011; Lindstrom et al., 2011). The concerns raised around the year 2000 regarding their toxicity, persistence, and global spread led to restrictions and voluntary phase-out of the most emergent PFASs. Perfluorooctane sulfonic acid (PFOS) was phased out by the major producer 3M Company, and a few years later the voluntary stewardship program was initiated by US EPA which aimed to eliminate long-chained perfluorocarboxylic acids (PFCAs) (3M

Company, 2000; US EPA, 2006). Concurrent with decreased manufacturing and use of the aforementioned PFASs, production of shorter-chained homologues, fluorotelomer compounds, for instance polyfluoroalkyl phosphate esters (PAPs), as well as new groups of PFASs such as perfluoropolyethers (PFPEs) have increased (Wang et al., 2013). Also, a geographical shift has occurred, with decreasing PFOS production in Europe and North America and increasing PFAS production in Asia, comprising continuous production of PFOS (Wang et al., 2014a).

PFOS and PFCAs (C9–C14) are persistent, resulting in bioaccumulation and biomagnification in aquatic and terrestrial food webs (Kelly et al., 2009; Tomy et al., 2009; Muller et al., 2011; Xu et al., 2014). Therefore, birds of prey are suitable for environmental biomonitoring. Since the phase-out of PFOS, temporal trend studies have shown various trends of PFASs in wild birds. For example, some studies of birds of prey have shown decreasing PFOS levels (Ahrens et al., 2011), or a peak around 2000 followed by a

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decline (Verreault et al., 2007; Holmstrom et al., 2010; Miller et al., 2015), while other studies have observed unaltered PFOS levels (Braune and Letcher, 2013; Miller et al., 2015). The variation observed between studies is likely due to their difference in location, as diverging trends have been seen within the same species when sampled in separate areas. An example is herring gull from the Baltic Sea for which PFOS increased during the entire study period 1991–2008, while in the same study a concentration peak was observed in 1994–2002 for herring gull from the North Sea (Rudel et al., 2011). Longer-chained PFCAs in bird eggs tend to increase globally in both marine, freshwater and terrestrial environments (Holmstrom et al., 2010; Ahrens et al., 2011; Braune and Letcher, 2013; Route et al., 2014). Most studies have focused on species in the marine environment. However, monitoring the freshwater and terrestrial environment provides a more accurate representation of recent exposure. In the marine food web, slow oceanic transport of persistent PFASs is a significant source of exposure, but integrates both historic and recent contamination (Prevedouros et al., 2006). Long-range atmospheric transport is of greater importance in the terrestrial and freshwater environments, since it is occurring at a faster rate than oceanic transport. Consequently, larger annual variations in the terrestrial environment have been observed compared to the marine environment (Bustnes et al., 2015). Volatile precursor compounds that are atmospherically transported can degrade to persistent PFASs (Ellis et al., 2004; Martin et al., 2006; Prevedouros et al., 2006). Common transformation intermediate products from several telomer precursors are fluorotelomer carboxylic acids (FTCAs) and fluorotelomer unsaturated carboxylic acids (FTUCAs). Another route of exposure in the freshwater and terrestrial environments is point-source emissions from waste-water treatment plants (WWTP), aqueous fire-fighting foam (AFFF) contamination, landfills, and manufacturing plants (Ahrens and Bundschuh, 2014). The influence of exposure from precursor compounds to the environment is not well studied. Differentiation between the food webs is important when assessing trends and patterns of PFASs. Stable isotope analysis of carbon and nitrogen ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) is a useful tool for elucidating dietary source and trophic level, thus illustrating how the food web is structured (Kelly, 2000). The $\delta^{15}\text{N}$ value is associated with trophic level, where a $\delta^{15}\text{N}$ shift of approximately 2–3‰ reflects one trophic level within a food web, while the $\delta^{13}\text{C}$ value indicates feeding from the terrestrial/freshwater or marine environment.

In this study, we investigated recent precursor exposure of PFASs and effects of production shifts by analyzing PFAS levels and assessing the composition profiles in bird eggs from the terrestrial and freshwater environments. Several PFAS groups were targeted; persistent PFASs that exist in their stable end form such as PFCAs and perfluorinated sulfonic acids (PFSAs), precursor compounds that are eventually subject to degradation (diPAPs, perfluorooctane sulfonamides (FOSAs), perfluorooctane sulfonamideethanols (FOSEs), one fluorotelomer sulfonic acid (FTSA)), and intermediates (FTCAs, FTUCAs), formed during precursor transformation, together with stable isotopes of carbon and nitrogen. Eggs from three raptor species in terrestrial and freshwater environments were analyzed; tawny owl, common kestrel, and osprey. For the osprey samples a temporal trend was studied from 1997–2001 to 2013.

2. Materials and methods

2.1. Samples

Bird eggs (unhatchable) from three species were included in this study; osprey (*Pandion haliaetus*) common kestrel (*Falco*

tinnunculus), and tawny owl (*Strix aluco*). Osprey is a migratory bird and spend the winter season in West Africa, and feed mainly on fish (Glass and Watts, 2009). Common kestrel (*Falco tinnunculus*) is a migratory bird and spend the winter season in southwestern Europe during winter season, and feed on rodents (Costantini et al., 2005). Tawny owl is a non-migratory species that feed mainly on rodents (Solonen and Karhunen, 2002). Ten osprey eggs from each period 1997–2001, 2007–2008, and 2013 were analyzed. A number of 40 eggs of common kestrel from 2014 were analyzed. Ten eggs of tawny owl from 2014 were analyzed. Samples were collected from different parts of Sweden in rural areas (Fig. S1, Table S1 and S2 SI).

2.2. Chemicals

Standards of native PFCAs (C4–C14), ^{13}C -labeled PFCAs (C4, C6, C8–C12), native PFSAs (C4, C6, C8, C10), technical PFOS, $^{13}\text{C}/^{18}\text{O}$ -labeled PFSAs (C6, C8), native and ^{13}C -labeled diPAPs (6:2, 8:2), native and ^{13}C -labeled FTUCAs (6:2, 8:2, 10:2), native FTCAs (5:3, 7:3), native and labeled PFOSA, N-MeFOSA, N-EtFOSA, N-MeFOSE, N-EtFOSE, native and ^{13}C -labeled 6:2 FTSA were obtained from Wellington Laboratories (Guelph, ON, Canada). Standard of native 10:2 diPAP was obtained from Chiron (Trondheim, Norway). HPLC-grade methanol and acetonitrile were purchased from Fisher Scientific (Ottawa, Canada), and Supelclean ENVI-carb (120/400 mesh) was purchased from Supelco (Bellafonte, PA, USA). Deionized water was from a purification system (18.2 Ω , Merck Millipore, Darmstadt, Germany) Ammonium hydroxide, glacial acetic acid, and sodium acetate were purchased from E. Merck (Darmstadt, Germany). Ammonium acetate was purchased from Fluka (Steinheim, Germany). 1-methyl piperidine was purchased from Sigma Aldrich (Stockholm, Sweden).

2.3. Extraction and clean-up

An amount of 0.25 g thawed homogenate from one egg was added to a 15 mL polypropylene tube and spiked with labeled isotopic internal standards (2 ng PFCAs, PFSAs, FTUCAs, FTCAs, and FTSAs, 8 ng FOSAs, FOSEs, and diPAPs), followed by extraction with 4 mL acetonitrile. The sample was sonicated for 15 min, shaken for 15 min and centrifuged at 8000 g for 15 min. The supernatant was transferred to new polypropylene tubes with 50 mg ENVI-carb and 100 μL glacial acetic acid. Another volume of 4 mL acetonitrile was added to the sample and the extraction procedure was repeated and the aliquots were combined. After evaporation under nitrogen, the extracts were filtered (0.2 μm hydrophilic polypropylene filters) into LC-vials and the final volume was 200 μL . Labeled isotope performance standards were added and the extract was split into one fraction with final concentration of 80% acetonitrile and 20% Milli-Q water with 1-methylpiperidine (5 mM) and ammonium acetate (2 mM) for analysis of diPAPs and one fraction with 40% acetonitrile and 60% Milli-Q water with ammonium acetate (2 mM) for analysis of PFCAs, PFSAs, FTUCAs, FTCAs, FOSAs, FOSEs, and FTSAs. One procedural blank and quality control sample were included in each batch and treated in the same way as the samples.

2.4. Instrumental analysis

For PFAS analysis two systems were used; 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 mass spectrometer (Waters Corporation, Milford, USA). A guard column (PFC isolator, Waters Corporation, Milford, USA) was inserted between the pump and the injector to prevent contamination from the system. The analytes were

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