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Contrasting long term temporal trends in perfluoroalkyl substances (PFAS) in eggs of the northern gannet (*Morus bassanus*) from two UK colonies

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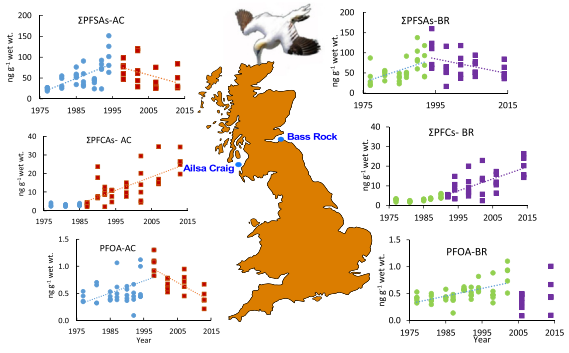
HIGHLIGHTS

- Long-term (>35 years) analyses of PFAS concentrations in gannet eggs from a North Sea and a Irish Sea colony.
- PFOS dominated the PFAS profile in eggs from both colonies.
- Overtime, the ∑PFSSs first rose and then fell and ∑PFCAs remained unchanged and then rose.
- PFOS and PFOA concentrations increased in early years but are now declining.
- Long-chain odd PFCAs concentrations in eggs are still increasing.

GRAPHICAL ABSTRACT



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ABSTRACT

We compared long-term (1977 to 2014) trends in concentrations of PFAS in eggs of the marine sentinel species, the Northern gannet (*Morus bassanus*), from the Irish Sea (Ailsa Craig) and the North Sea (Bass Rock). Concentrations of eight perfluorinated carboxylic acids (PFCAs) and three perfluorinated sulfonates (PFSAs) were determined and we report the first dataset on PFAS in UK seabirds before and after the PFOS ban. There were no significant differences in ∑PFAS or ∑PFSAs between both colonies. The ∑PFSAs dominated the PFAS profile (>80%); PFOS accounted for the majority of the PFSAs (98–99%). In contrast, ∑PFCAs concentrations were slightly but significantly higher in eggs from Ailsa Craig than in those from Bass Rock. The most abundant PFCAs were perfluorotridecanoate (PFTriDA) and perfluoroundecanoate (PFUnA) which, together with PFOA, comprised around 90% of the ∑PFCAs.

The ∑PFSAs and ∑PFCAs had very different temporal trends. ∑PFSAs concentrations in eggs from both colonies increased significantly in the earlier part of the study but later declined significantly, demonstrating the effectiveness of the phasing out of PFOS production in the 2000s. In contrast, ∑PFCAs concentrations in eggs were constant and low in the 1970s and 1980s, suggesting minimal environmental contamination, but residues subsequently increased significantly in both colonies until the end of the study. This increase appeared driven by rises in long chain compounds, namely the odd chain numbered PFTriDA and PFUnA. PFOA, had a very different temporal trend from the other dominant acids, with an earlier rise in concentrations followed by a decline in the last 15 years in Ailsa Craig; later temporal trends in Bass Rock eggs were unclear.

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Although eggs from both colonies contained relatively low concentrations of PFAS, the majority had PFOS residues that exceeded a suggested Predicted No Effect Concentration and ~ 10% of the eggs exceeded a suggested Lowest-Observable-Adverse-Effect.

1. Introduction

Perfluoroalkyl substances (PFAS) are man-made compounds, produced since the 1950s and, historically considered unreactive. They are industrially manufactured by electrochemical fluorination (which produces linear and branched PFAS) and by telomerisation (which produces straight chain compounds only). The PFAS class includes a large number of compounds with 4 to 18 carbon atoms and a hydrophilic functional group (Buck et al., 2011; Kissa, 2001), with perfluorooctane sulfonic acid (PFOS) and perfluooctanoic acid (PFOA) being the best known.

PFAS are chemically and thermally stable due to their chemical structure and, because of their surfactant properties, they provide stain, water and oil resistance (Kissa, 2001). They have been extensively used in a diverse range of industrial and domestic applications (Giesy and Kannan, 2002; Prevedouros et al., 2006; Renner, 2001).

The presence of PFAS in the environment originates from direct usage and from environmental transformation of other labile perfluoralkyl compounds (Giesy and Kannan, 2001; Zhao et al., 2015). Due to their chemical stability, they are recalcitrant to degradation and metabolism and can be subject to long-range transportation (Kannan et al., 2005). Consequently, they have become global pollutants and are present in abiotic and biotic matrices (Pico et al., 2011) including air, water, sediments and wildlife such as birds and marine mammals (Giesy and Kannan, 2001; Liu et al., 2009; Miller et al., 2015; Nakata et al., 2006; Norden et al., 2016; Su et al., 2017; Yamashita et al., 2005). PFAS are protein binding and bioaccumulative (when >7 carbons), with the potential for bioaccumulation increasing with chain length (Müller et al., 2011; Tomy et al., 2009; Xu et al., 2014). PFOS is considered the most important PFAS because of its high volume production, toxicity, widespread distribution and persistence.

Several studies have shown that PFOS can be toxic to birds and mammals, affecting thyroid and liver function, and producing hepatocellular adenomas and peroxisome proliferation (Molina et al., 2006; Austin et al., 2003; Lau et al., 2004). PFAS, because of their persistence, widespread distribution, bioaccumulation potential and toxicity are considered compounds of concern (Martin et al., 2004; Tomy et al., 2004). The main manufacturer (3 M) voluntarily phased out the production of PFOS, PFOA and related compounds in 2000 and many countries have now restricted their use, including the European Union (European Union, 2006). PFOS and its salts were also listed in 2009 in the Stockholm Convention (annex B) as a POP (due namely to its persistent and bioaccumulative properties), ensuring restriction of production in signatory countries (UNEP, 2009). However, PFOS is still produced in Southeast Asia, especially in China (Lim et al., 2011).

PFOS and PFOA are widely distributed in aquatic ecosystems and therefore bioaccumulation and effects in top marine predators is a concern. The highest levels of PFAS have been found in fish-eating animals in industrialised areas (Lopez-Antia et al., 2017). Fish-eating birds are considered particularly valuable sentinels of changing exposure to, and risk from, these contaminants; the magnitude of accumulated residues can change swiftly and sensitively in response to changes in environmental concentrations (Crosse et al., 2012).

Levels of PFAS in seabirds have been reported in Europe (Sun et al., 2019; Escoruela et al., 2018; Faxneld et al., 2016; Norden et al., 2013; Verreault et al., 2005), Canada (Braune et al., 2014; Gewurtz et al., 2018; Miller et al., 2015), USA (Letcher et al., 2015; Sedlak et al., 2017) and elsewhere (Chu et al., 2015). However, as far as we are aware there are few or no data on concentrations in seabirds for the UK.

In the current study, we report novel and unique data for two PFAS groups, perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonates (PFSAs) to which PFOA and PFOS belong, respectively (Table 1). We measured concentrations in the fresh eggs of a sentinel species, the northern gannet *Morus bassanus*; the eggs were from two UK island colonies, one in the Eastern Atlantic, the other in the North Sea. We used eggs because they are considered a favourable matrix for monitoring given its consistent composition. In the case of income breeders like the gannet, contaminants in seabird eggs reflect the pollutant intake by females foraging close to the colony prior to laying, with previous winter intake being a minor contribution to the total load contamination in the eggs (Becker et al., 1998; Pereira et al., 2009). Our objectives were to: 1) determine how the concentrations of PFAS in gannet eggs in the two colonies changed over a period of 37 years; 2) investigate how temporal trends varied between individual PFSAs and PFCAs, and 3) - examine spatial variation of contamination as reflected by differences in egg concentrations between colonies.

2. Materials and methods

2.1. Sample collection

Gannet eggs were collected from Ailsa Craig (AC), a granite island situated in the outer side of the Firth of Clyde on the west coast of Scotland, and from Bass Rock (BR), located in the outer part of the Firth of Forth on the east coast of Scotland, in the North Sea. Details on the colonies can be found in Pereira et al. (2009).

Breeding gannets from both colonies can feed locally but also in a range of 150 km (Hamer et al., 2001) and the colony specific travel distance depends on density- dependent competition (Wakefield et al., 2013). However, gannets do not fly overland to feed and there is no overlap between feeding areas of AC and BR colonies; gannets from BR forage in the North Sea, whereas birds from AC feed in waters to the west of Britain (Wakefield et al., 2013). Gannets feed mostly in lipid-rich pelagic fish such as mackerel, herring and sandeel (Hamer et al., 2000), but they also can feed on discards from commercial fishing vessels (Hamer et al., 2001).

The eggs were collected under licence as part of the long-term monitoring programme Predatory Bird Monitoring Scheme (PBMS; http://pbms.ceh.ac.uk). Four to six (most often five) fresh eggs were taken during laying or early incubation period, from separate nests at each

Table 1
List of compounds (and acronyms) analysed.

Compound	Carbon	Abbreviation
Perfluorinated sulfonates (PFSAs)		
Perfluorohexane sulfonic acid	C6	PFHxS
Perfluorooctane sulfonic acid	C8	PFOS
Perfluorodecane sulfonic acid	C10	PFDS
Perfluorinated carboxylic acids (PFCAs)		
Perfluorobutanoic acid	C4	PFBA
Perfluorooctanoic acid	C8	PFOA
Perfluorononanoic acid	C9	PFNA
Perfluorodecanoic acid	C10	PFDA
Perfluoroundecanoic acid	C11	PFUnA
Perfluorododecanoic acid	C12	PFDoA
Perfluorotridecanoic acid	C13	PFTriDA
Perfluorotetradecanoic acid	C14	PFTeDA

colony. Sampling was carried out every two to four years between 1977 and 2014. In total, 57 eggs from BR and 54 from AC were analysed.

Once collected, egg weight, length and breadth were measured and the eggs were then blown (so that the egg shell could be archived by a museum) or cracked open (for the last decade). The eggshells were washed, air-dried and reweighed; the egg contents were homogenised and stored in clean glass jars at -20 °C until analysed.

2.2. Chemical analysis

PFAS were analysed using a similar procedure to that described in Vicente et al. (2012) and information on the standards and reagents can be found in the SI. In summary, PFAS were extracted using solid-liquid extraction from homogenised whole eggs. Wet samples (1 g) were spiked with 50 ng of labelled internal standards (^{13}C-PFOS, and ^{13}C-PFOA, Wellington Laboratories, Canada) and incubated for 18 h at 4 °C. After incubation, 9 ml of acetonitrile was added and the samples were thoroughly mixed using a vortex. Samples were extracted in an ultrasonic bath for 10 min at room temperature. This procedure (vortex and ultrasonication) was repeated 3 times without solvent exchange.

Samples were then centrifuged at 2500 rpm for 5 min and the supernatant was collected and evaporated to dryness. The residue was resuspended in acetonitrile and incubated for 10 min in an ultrasonic bath. The extracts were cleaned by adding 25 mg of activated carbon and 50 μl of glacial acetic acid, which were vigorously mixed for 1 min. Samples were then centrifuged for a further 10 min at 10,000 rpm. The supernatant was transferred to a micro-vial, evaporated and reconstituted with 500 μl (10 mM water with ammonium acetate; and acetonitrile 1:1).

We analysed 8 perfluorinated carboxylic acids (PFCAs) and three perfluorinated sulfonates (PFSAs) (Table 1) using an ACQUITY Ultra Performance Liquid Chromatography (UPLC) system (Waters, USA) connected to a Triple Quadruple Mass Spectrometry Detector (Waters, UK) in negative electrospray ionisation. 10 μl were injected using an Acquity UPLC BEH C18 analytical column (1.7 μm particle size, 100 mm × 2.1 mm, Waters, USA) and an Acquity UPLC BEH C18 Column (1.7 μm particle size, 50 mm × 2.1 mm, Waters, USA) was used as a residue trap to remove any contamination from the mobile phase. The mobile phase consisted of (A) HPLC water with 10 mM ammonium acetate/methanol (80:20) and (B) acetonitrile with 10 mM ammonium acetate. Gradient elution started from 70%A and 30%B, increased to 90%B in 5 min and to 100%B in 0.10 min and held for 1 min, at a flow rate of 0.4 ml min^{-1}.

Perfluoro-n-(1,2,3,4-^{13}C4) octanoic acid (^{13}C-PFOA) and sodium perfluoro-1-(1,2,3,4-^{13}C4) octanesulfonate (^{13}C-PFOS), were used as surrogate standards for internal standard quantification of carboxylates and sulfonates, respectively. A calibration curve ranging from 0.001 to 0.5 μg l^{-1} concentration was linear ($R^2 > 0.99$) for all compounds. For quality control and assurance purposes, a blank was included in each batch and no traces of any compound were detected as all material used in the extractions and in the HPLC-MS/MS analysis were of polypropylene, the use of a trap column ensured no external contamination from the instrument. Recovery for the total procedure was calculated using spiked chicken eggs at a concentration of 50 ng g^{-1}. The average recoveries ranged between 72% and 144% for different compounds. The method limit of detection (LOD) was calculated using a chicken egg spiked at a concentration of 10 ng g^{-1} and using a signal to noise ratio of 3. The mean LODs for the PFCAs was 0.060 ng g^{-1} and ranged from 0.015 to 0.107 ng g^{-1}, while the LOD for PFSAs was 0.028, 0.084 and 0.137 ng g^{-1} for PFDS, PFHxS and PFOS, respectively.

2.3. Data analysis

Perfluorinated compounds concentrations are reported in ng g^{-1} wet weight (wet wt.). For statistical analyses and for the calculation of ΣPFCAs, ΣPFSAs and ΣPFAS; compounds below the limit of detection were assigned a zero value to ensure that the total concentrations were not overestimated (Crosse et al., 2012). PFAS concentrations were adjusted for desiccation by multiplying the concentrations by the total egg weight/volume ratio. Egg volume was estimated using the eq. $V = 0.51 \times LB^2$, where L is egg length and B is egg breadth (Hoyt, 1979). Some eggs were damaged on receipt and mean volume/weight ratios could not be calculated. In those cases, the mean volume/weight ratio for eggs received either that year or for the colony as a whole was used to adjust for desiccation.

Comparison of ΣPFCAs, ΣPFSAs and ΣPFAS between colonies was carried out by comparing annual median concentrations for the two colonies using a Wilcoxon matched pair test. Parametric analyses were not used because the underlying assumptions of homogeneity of variance and normality of residuals were not met.

Temporal trends in ΣPFCA and ΣPFSA concentrations in each colony were analysed using linear split-line regressions. The breakpoint was determined by using a non-parametric optimisation approach to minimise the sum of squared residuals based on 5 different parameters of interest: the intercept and slop of each regression line and the breakpoint (Tipping et al., 2013). Inter-colony comparisons of the slopes and intercepts of the linear regressions for the various compounds were conducted using analysis of covariance (Ancova).

3. Results

3.1. PFAS profiles

The data associated with this study is available from the UKCEH Data Catalogue (https://catalogue.ceh.ac.uk/documents) and can be identified from their digital object identifier (https://doi.org/10.5285/43487d30-ba23-424e-a2bb-d04dd121875c).

3.1.1. PFSAs

Of the three PFSA analysed, PFHxS and PFOS were present in all the eggs from both colonies but PFDS was only detected in two eggs, both from AC (4% of the total analysed from that colony). Annual median ΣPFSAs concentrations ranged between 16.5 and 165 ng g^{-1} wet wt.; Fig. 1). PFOS dominated the PFSA profile, with concentrations reaching 163 ng g^{-1} wet wt. and comprising approximately ~99% of the ΣPFSAs concentrations (Fig. 1). There was no significant inter-colony variation in either PFOS concentration or ΣPFSAs ($W = -28.00$; $P > 0.05$).

3.1.2. PFCAs

Of the 8 PFCAs (C4 to C14; Table 1) that we quantified, each was detected in a similar proportion of eggs in both colonies, with the exception of PFDoA which was present in twice as many eggs from AC (48% of the total analysed) than from BR (23%). PFOA and PFTriDA were the most frequently detected PFCAs, occurring in almost all (98 to 100%) eggs. PFUnA was detected in ~60% of the eggs and the remaining acids were present in between 20% to 40% of the eggs, with the exception of PFTeDA, which was only present in 10% of samples.

Summed PFCAs concentrations ranged between 2.0 and 34.5 ng g^{-1} wet wt. in eggs from AC and 1.6 and 26.4 ng g^{-1} wet wt. in BR eggs (Fig. 1). A Wilcoxon matched (by year)–paired test showed that the $\sum$PFCAs in AC were slightly, and just significantly, higher than that in BR ($W = 50$; $P = 0.024$).

PFTriDA was present in the greatest concentrations in both colonies (Fig. 1; Table S1), comprising ~60% of ΣPFCAs with medians of 4.3 and 3.9 ng g^{-1} wet wt. in AC and BR, respectively. The next most abundant compounds were PFUnA and PFOA with medians of 2.6 and 0.50 ng g^{-1} wet wt. in AC and 0.48 and 0.47 ng g^{-1} wet wt. in BR, respectively. PFUnA comprised 25% of the ΣPFCAs in AC, and 11% in BR but approximately a quarter of eggs in each colony had higher concentrations of PFUnA than PFTriDA. Overall, these three compounds represented, on average, 90% and 82% of the ΣPFCAs concentration, in AC and BR, respectively (Fig. 1). The smaller chain PFBA and the longer chain PFTeDA comprised <3% of the ΣPFCAs concentration.

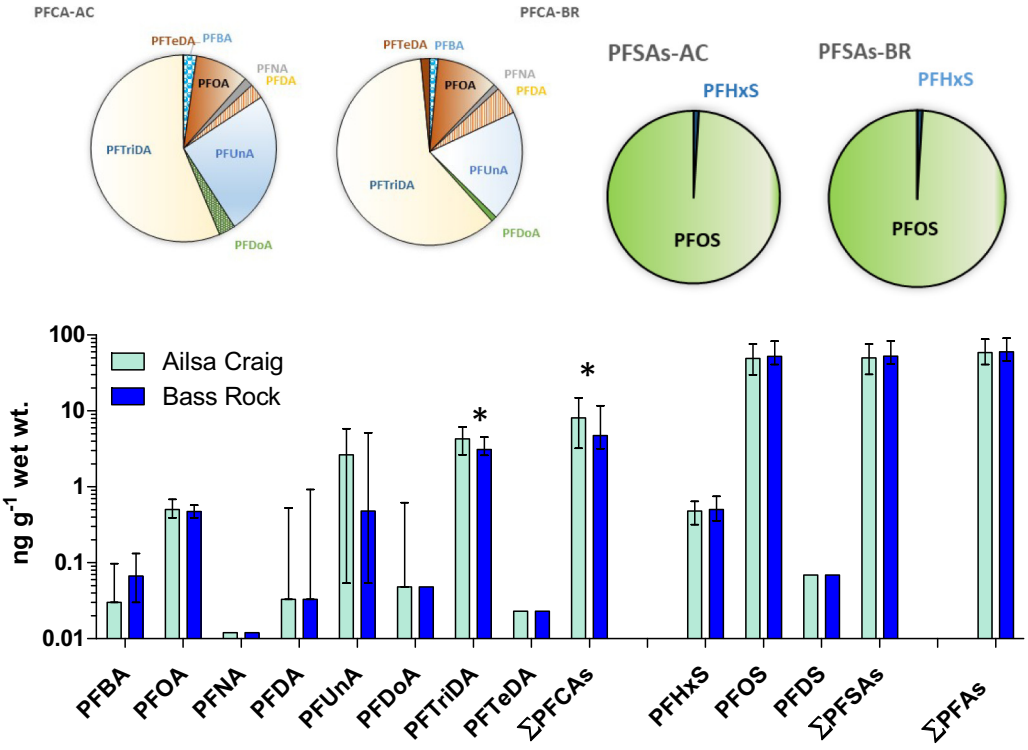

Fig. 1. Median (± Inter-Quartile Range) concentrations (ng g^{-1} wet wt.) of individual perfluoroalkyl substances, and the sum of perfluorinated carboxylic acids (∑PFCAs), sum perfluorinated sulfonates (∑PFSAs) and sum polyfluoroalkyl substances (∑PFAS) in gannet eggs from Alisa Craig and Bass Rock colonies collected between 1977 and 2014. (* represent inter-colony significant differences). Pie charts – proportion of individual acids and sulfonates in relation to the total PFCAs and PFSAs, respectively.

3.1.3. PFAS

The sum of all PFAS concentrations (ΣPFAS- comprising the ΣPFSAs and the ΣPFCAs) varied between 20.6 and 181.9 ng g^{-1} wet wt. and there were no significant differences between colonies (Wilcoxon Matched Pair: W = -14.00, P > 0.05; Table S1). The sulfonates accounted for 84% and 89% of the ΣPFAS observed in the AC and BR eggs, respectively, largely because of the high levels of PFOS.

A temporal analysis of the proportion of ΣPFSAs in relation to the ΣPFAS showed that although the ΣPFSAs predominated throughout the study, their proportion decreased in the last 20 years. In the first 20 years covered by the current study, PFSAs accounted for 92 to 96% of the ΣPFAS in eggs from both colonies (Fig. 2) but, from 1994 onwards, the proportion decreased and by 2014 comprised 62% and 73% of ΣPFAS in AC and BR eggs, respectively.

3.2. Temporal trends

3.2.1. PFSAs

Between 1977 and the mid-1990s the concentrations of ΣPFSAs increased significantly in both colonies (Table S2) and then declined linearly and significantly until 2014 (Table S2 and Fig. 3).

The statistically determined "breakpoint" after which concentrations started to decrease significantly was 1998 for AC and 1994 for BR. The rate of increase was 4.7 and 2.2 ng g^{-1} wet wt. per year and the rate of decline was 1.9 and 2.5 2 ng g^{-1} wet wt. per year for AC and BR, respectively. Neither the rate of increase ($F_{1, 59} = 0.22$, $P = 0.64$) or decline ($F_{1, 44} = 0.39$, $P = 0.54$) was significantly different between the colonies. By 2014, concentration of PFSAs were only slightly higher than in 1977. PFOS had an identical temporal profile to the ΣPFSAs, as did PFHxS (data not shown), suggesting that both compounds were used at the same time and subsequently declined at the same rate. The half-lives of PFOS in BR was 20.9 years and in AC 15.5 years.

3.2.2. PFCAs

In the mid-1970s, the ΣPFCAs concentrations were low (~ 3 ng g^{-1} wet wt.) and remained more or less constant in both colonies, indicating a general lack of exposure of gannets to PFCAs until the late 1980s. In the case of the longer-chain PFCAs these were completely absent in the early years with exception of PFTriDA (Fig. 4). After 1988 in AC and 1992 in BR, egg ΣPFCAs concentrations increased linearly and significantly until the end of the study (Tables S2; Fig. 4). The concentrations in AC started to rise significantly earlier than in BR ($F_{1, 71} = 8.58$, $P < 0.005$), suggesting that the bioaccumulation of these compounds occurred earlier in the North Sea than in the eastern Atlantic. The annual rate of increase was similar in both colonies ($F_{1,70} = 0.66$, $P = 0.418$).

We applied the same breakpoint year obtained for the ∑PFCAs to each individual compound. Of these, PFDA, PFUnA and PFTriDA increased linearly and significantly in eggs from both colonies over the last 25 years (Table S2). PFNA was undetected until 2002 and 2006 in AC and BR, respectively, after which the values increased and were the highest by the end of the study. Nonetheless, due to the limited number of measurements we did not fit a regression line to the data. The concentrations of these four compounds were still increasing at the end of the period covered by the current study (Fig. 4). There were no significant time trends for the other PFCAs. This suggests that PFNA, PFDA, PFUnA and PFTriDA were driving the temporal rise in ∑PFCAs. The rates of increase of these compounds did not differ significantly between colonies.

The temporal profile of PFOA contrasted with that of the longer chain-compounds (Fig. 5). PFOA levels increased significantly in AC eggs until 1998 and in BR until 2002 (Fig. 5; Table S2). In AC eggs, PFOA then significantly declined between 1998 and 2013 (Table S2). The rate of decline in concentration was 30% in 15 years and the decline only started 10 years after levels of the longer chain acids started to increase. No temporal trend could be found in PFOA residues in BR eggs between 2002 and 2014 (Fig. 5).

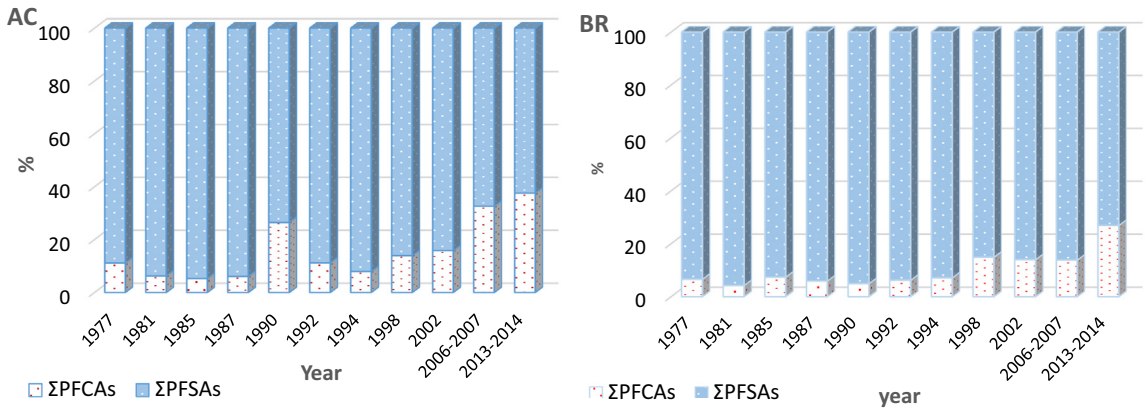

Fig. 2. Temporal trend of the proportion of the sum of perfluorinated carboxylic acids (∑PFCAs) and the sum perfluorinated sulfonates (∑PFSAs) in relation to the total compounds analysed in gannet eggs from Alisa Craig (AC) and Bass Rock colonies (BR).

4. Discussion

4.1. PFAS profiles

4.1.1. PFSAs

The high proportion of PFOS (99% of the ∑PFSAs) in the gannet eggs was expected given that this is the most commonly detected fluorinated compound in biota everywhere (Ahrens et al., 2009; Braune and Letcher, 2013; Fliedner et al., 2012; Houde et al., 2006; Reiner et al., 2011). The predominance of PFOS in the environment is likely the result of its widespread intentional use combined with it also being a product of the metabolism of other compounds, such as PFOSA (perfluorooctanesulfonamide). Furthermore, PFOS biomagnifies in the aquatic foodweb (Loi et al., 2011; Powley et al., 2008) and thus high levels are to be expected in top predators such as fish-eating birds.

The dominance of PFOS in relation to other PFAS observed here was similar to that reported elsewhere in other seabird eggs from Europe and Canada (Eriksson et al., 2016; Faxneld et al., 2016; Letcher et al., 2015; Miller et al., 2015). Although PFOS is the predominant PFAS in biota, concentrations can vary markedly between species and particularly between trophic pathways. For example, very high concentrations (up to 1.3 μg/g wet wt.) have been detected in guillemot (*Uria aalge*) eggs from the Baltic Sea whereas levels in the peregrine falcon (*Falco peregrinus*) eggs, were considerably lower (83 ng g^{-1} wet wt.; Holmstrom et al., 2005; Holmstrom et al., 2010). This suggests that marine food web is potentially more at risk of exposure to higher levels of PFAS than the terrestrial one, given that the falcons in the breeding season feed mostly on terrestrial prey.

However, the concentrations reported here in the gannet eggs were within the range observed in other seabirds eggs (Eriksson et al., 2016; Fliedner et al., 2012; Gebbink et al., 2011; Verreault et al., 2007; Verreault et al., 2005; Zapata et al., 2018), but lower than the maximum concentrations observed in the eggs of other species (Elliott et al., 2014; Gewurtz et al., 2018; Norden et al., 2013; Rudel et al., 2011). These differences in PFOS concentrations observed in marine seabirds, likely reflect the trophic level position, combined with local sources of contamination.

PFHxS, in contrast with PFOS, was detected in very low concentrations and making around 1% of the ∑PFSAs, this is similar to what was observed by Letcher et al. (2015). Low concentrations in top predators are expected due to the low bioaccumulative potential of short-chain PFAS. Nevertheless, PFHxS was present in all our eggs, agreeing with data reported in osprey eggs (Eriksson et al., 2016). The presence of environmental PFHxS is to be expected given that it has been intentionally manufactured and is also a by-product of PFOS degradation.

4.1.2. PFCAs

∑PFCAs in both colonies varied between 1.6 and 34.5 ng g^{-1} wet wt. These values were within the same or lower order of magnitude than that reported elsewhere for other fish-eating birds. In herring gull (*Larus argentatus*) eggs from various Canadian lakes, concentrations ranged between 14.8 and 118 ng g^{-1} wet wt. (Letcher et al., 2015); in Swedish osprey (*Pandion haliaetus*) eggs the median was 27.7 ng g^{-1} wet wt. (Eriksson et al., 2016) and in US tern (*Hydroprogne caspia*) eggs the mean was 131 ng g^{-1} wet wt. (Su et al., 2017). Therefore, UK gannets have comparable amounts of these compounds to other offshore bird species across the world.

∑PFCAs residues in eggs from AC were marginally, but significantly higher than those in eggs from BR, contrasting with the ∑PFSAs where no colony differences were found. Spatial differences in ∑PFCAs were

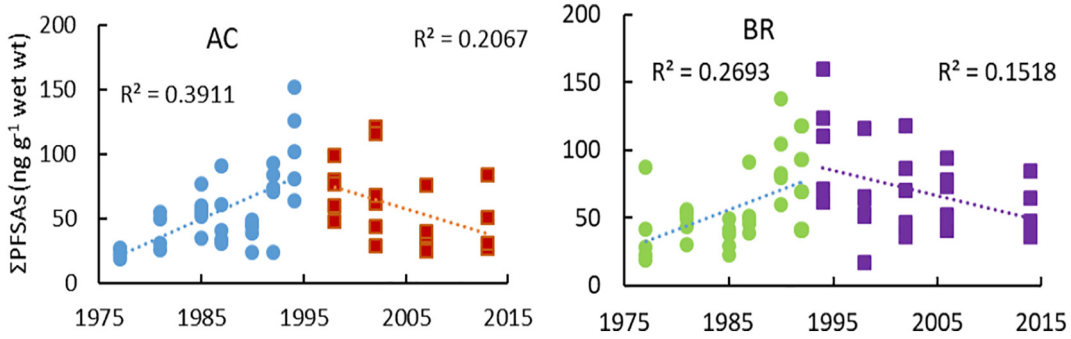

Fig. 3. Temporal trends (split line regression models wet wt. concentrations) ΣPFSAs concentrations in gannet eggs from Ailsa Craig (AC) and Bass Rock (BR). Data with different symbols distinguish the years before and after the breakpoints in the regression mode of the ΣPFSAs.

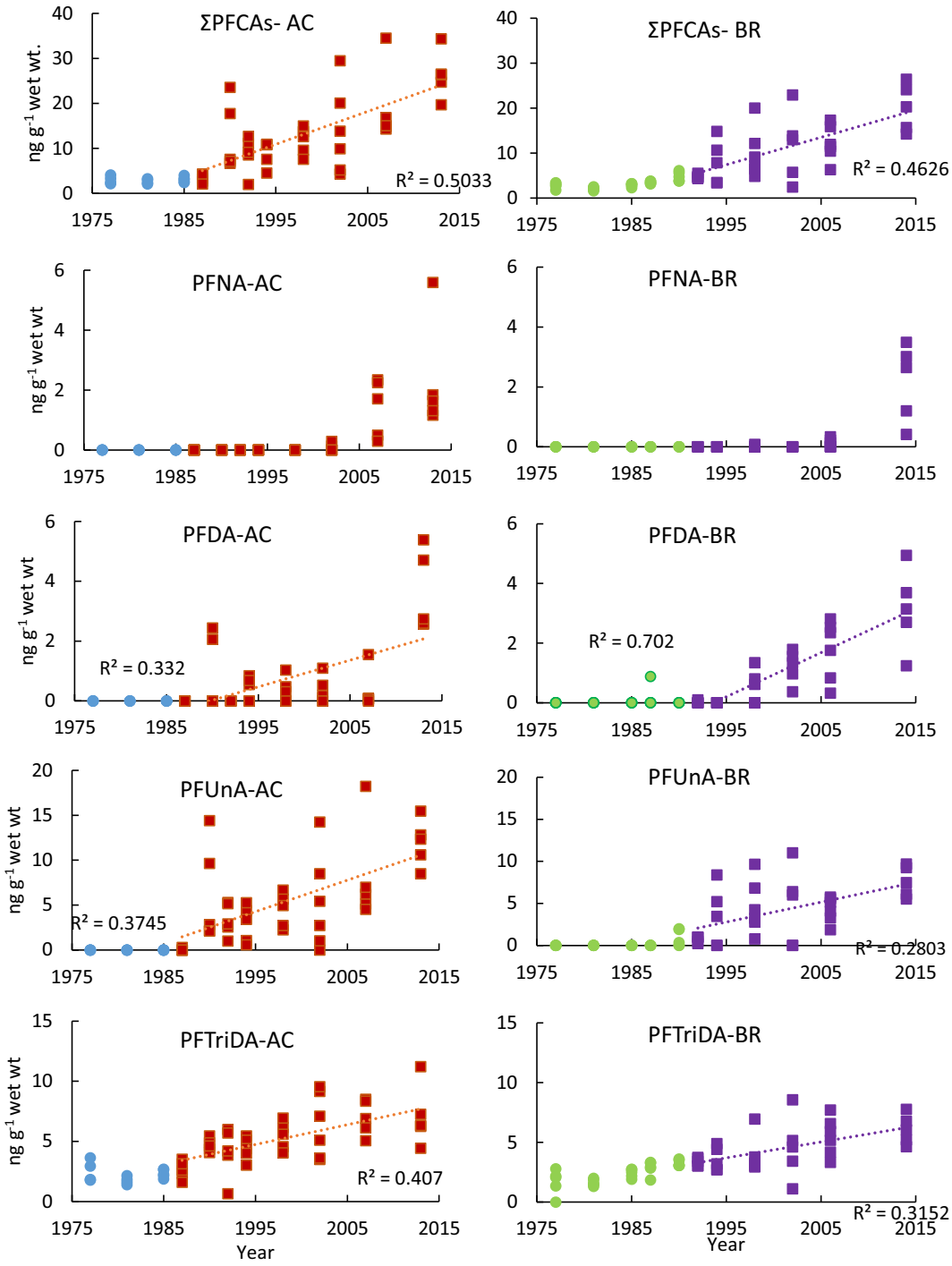

Fig. 4. Temporal trends (split line regression models wet wt. concentrations) in PFNA, PFDA, PFUnA, PFTriDA and ΣPFCAs concentrations in gannet eggs from Ailsa Craig (AC) and Bass Rock (BR). Data with different symbols distinguish the years before and after the breakpoints in the regression mode of the ΣPFCAs.

probably the result of differences between the colonies in the birds diet, given the varied diet on pelagic fish combined with discards from fishing boats, which can also contain demersal fish (Pereira et al., 2009), and/or different environmental concentrations in prey due to possible diverse industrial and urban usage. Both colonies also forage close the costal urban centres (Wakefield et al., 2013), which play an important role in the environmental contaminant load and consequently affect inter-colony variation.

We found no colony differences in the concentrations of the most frequently detected compounds, with PFOA and PFTriDA present in practically every egg and PFUnA in 60% of the samples. The common presence of long-chain PFCAs in the eggs was expected given that they are more bioaccumulative than short-chain ones (Route et al., 2014). Compounds with chain lengths of C10–C14 (PFDA to PFTeDA) have the highest reported bioaccumulation potential (Ng and Hungerbuhler, 2014) with accumulation attributable to their hydrophilic properties (Eriksson et al., 2016). Consistent with this, we found that long-chain PFCAs, and in particular of C11 and C13, together comprised 80% of the total PFCA concentration in gannet eggs (Fig. 1). Similar findings were observed in a variety of seabird eggs (Braune and Letcher, 2013; Letcher et al., 2015; Miller et al., 2015; Norden et al., 2013; Tartu et al., 2014; Verreault et al., 2007). A study looking at

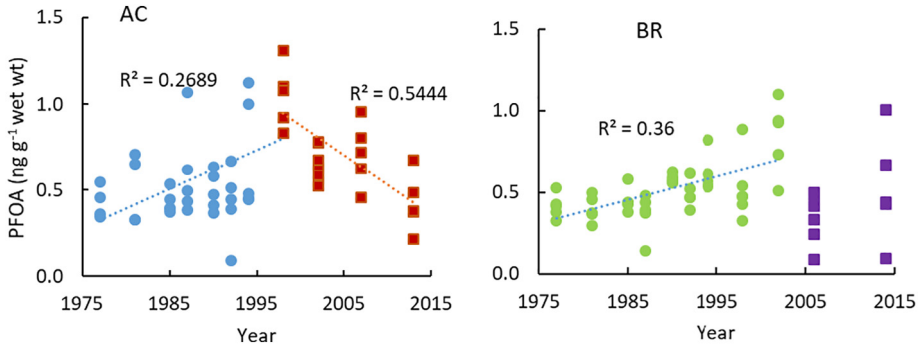

Fig. 5. Temporal trends (split line regression models wet wt. concentrations) in PFOA concentrations in gannet eggs from Ailsa Craig (AC) and Bass Rock (BR). Data with different symbols distinguish the years before and after the breakpoints in the regression mode of the ΣPFCAs.

PFCAs in gulls livers and their eggs revealed that C8–C11 dominated in livers whereas C9–C15 dominated in the entire egg clutch (Gebbink and Letcher, 2012). Therefore, *in ovo* enrichment could at least explain, in part, the predominance of PFUnA and PFTriDA in the present and other studies.

The high concentrations of the C11 and C13 compounds reveals that not only do long-chain compounds dominated the PFCA profile, but there is also a predominance of odd over even long-chain compounds. This pattern in PFCAs is characteristic of residues in eggs of marine (but not freshwater; Eriksson et al., 2016) birds from pristine areas (Houde et al., 2006) and has been considered to be the result of atmospheric transport, oxidation and deposition of precursors (Houde et al., 2006). Even numbered fluorotelomer-based precursor compounds degrade to odd and even numbered fluorinated acids with a similar yield consequently increasing the proportion of odd-numbered PFCAs (Armitage et al., 2009).

The absence of large inputs of direct sources of these compounds is also indicated by the low concentrations of PFDA (C10) and PFNA (C9). These are usually detected in high levels in eggs of various birds in coastal, urban and heavily industrial areas (Letcher et al., 2015; Miller et al., 2015; Sedlak et al., 2017). Consequently, this suggests that gannets are feeding in relatively pristine areas and consequently are not particularly affected by any large local sources of contamination.

Although PFOA was present in all samples, its concentrations were low (Fig. 1), which is in agreement with results obtained in herring gulls (*Larus argentatus*) eggs (Letcher et al., 2015) and white-tailed sea eagles (*Haliaeetus albicilla*) eggs (Faxneld et al., 2016). PFOA (as well as other short chain acids) is highly soluble in water and has been consistently detected at high concentrations in river and lake water samples (Ahrens et al., 2011; Lam et al., 2014). Its small contribution to the total concentration in eggs is most likely linked to its low bioaccumulation properties. Consequently, offshore birds accumulate lower levels of PFOA than those located near urban areas (Miller et al., 2015) or than non-predatory birds (Barghi et al., 2018). Differences in the contribution of PFOA to the ∑PFCAs between predatory and non-predatory birds has been attributed to differences in bioaccumulation factors based on toxicokinetics, especially elimination half-lives, or due to precursor degradation along the foodweb (Gebbink et al., 2016).

4.2. Temporal trends

4.2.1. PFSAs

In both colonies, ∑PFSAs increased for two decades peaking in the mid-1990s and subsequently declined. The identical temporal profiles for AC and BR suggest that the marine foodwebs in the East and West Coast of Scotland were influenced by comparable levels of input and bioaccumulation. The temporal profiles of PFOS, PFHxS and PFDS were all alike and similar to that reported by Faxneld et al. (2016) in white-tailed sea eagles (*Haliaeetus albicilla*) eggs. These profiles reflect the time periods over which these compounds were intentionally manufactured and were also produced as a by-product of PFOS manufacture (Benskin et al., 2010).

The decline in PFOS in gannet eggs was likely linked to the voluntary phase out of PFOS and its precursors by 3 M in the beginning of 2000s in the USA and Europe (EPA., 2006; Gewurtz et al., 2018). This reduction and follow up ban on manufacture may have contributed to the rapid decline of this compound in the eggs of both colonies, with values declining even before the ban was fully implemented. Furthermore, both colonies are situated in close proximity to former sites of sewage disposal. Dumping of sewage in the North and Irish Seas stopped in 1998 (Webster et al., 2008) and this could have also contributed to the decline in PFOS concentrations in the gannet eggs. Post phase-out declines in PFOS residues in eggs have similarly been reported in a variety of species from elsewhere (Ahrens et al., 2011; Gebbink et al., 2011; Holmstrom et al., 2005; Holmstrom et al., 2010; Kratzer et al., 2011; Letcher et al., 2015; Miller et al., 2015; Roos et al., 2013; Route et al., 2014). The estimated half-life of PFOS in gannets eggs is within the same order of magnitude as those reported in rhinoceros auklets (*Cerorhinca monocerata*) eggs (12.7 and 21 years; Miller et al., 2015) and in herring gulls (*Larus argentatus*) eggs (19.5 years; Gebbink et al., 2011).

Although, the phasing out of PFOS and regulatory interventions can evidently lead to a decrease in exposure and accumulation in biota, such legislation has not been uniformly effective worldwide. PFOS residues have not declined in populated areas, which is thought to be due to the continual emissions to the environment from consumer products (Liu et al., 2014). Furthermore, no noticeable changes have been observed in PFOS levels in eggs of some species (Braune and Letcher, 2013; Eriksson et al., 2016; Holmstrom et al., 2010; Miller et al., 2015) and this has been linked to emissions from historically contaminated sites (Eriksson et al., 2016) and large scale production by China since 2003 (Lim et al., 2011).

4.2.2. PFCAs

In contrast to ∑PFSAs, ∑PFCAs concentrations in the gannet eggs were low and remained unchanged in the first 2 decades of analyses, revealing that these compounds were absent from the environment where these birds were feeding. However, in the late 1980s (AC) and early 1990s (BR), egg concentrations started to increase and continued to rise until the end of this study, by which time PFCAs comprised 25–40% of the ∑PFAS concentration (Fig. 2). Although this increase began later in the North Sea than the Eastern Atlantic, we found no significant differences between colonies in the rates of increase. A rise in ∑PFCAs in the last decades has also been reported in the eggs from four Great Lakes herring gull colonies (Gebbink et al., 2011) and in Canadian auklets and petrels (Miller et al., 2015). In herring gull eggs from Norway, ∑PFCAs increased between 1983 and 1993, and then either continued to weakly increase or levelled off (Verreault et al.,

2007). Overall, this increase in ΣPFCAs is probably linked to the rise in the manufacture of fluorotelomer-based fluorinated compounds, such as perfluoroalkyl phosphates or FTOHs (Gebbink et al., 2011).

The temporal profile in the ∑PFCAs was mainly driven by two predominant compounds, PFUnA and PFTriDA, as well as by PFDA. All three had temporal profiles that matched that of the ∑PFCAs, and together with PFNA, were still increasing at the end of this study in both colonies. Other authors have reported similar findings regarding the increment in the temporal contributions of PFUnA and PFTriDA (Braune and Letcher, 2013; Fliedner et al., 2012; Miller et al., 2015). PFUnA and PFTriDA were not intentionally produced but their wide environmental distribution is probably attributable to direct sources, resulting from impurities in PFOA and PFNA, as well as indirect sources, such as atmospheric transport and degradation of precursors such as the ammonium salt of PFNA (Buck et al., 2011). The rise in these compounds over the last decades roughly coincides with the decline in PFOS usage, suggesting a switch to other fluorinated compounds.

The temporal distribution of PFOA was distinct from the ∑PFCAs and other individual PFCAs, probably as a result of different usage as well as bioaccumulation of this compound in relation to the longer-chain ones. PFOA has been used in EU mostly directly but indirect inputs also contribute to a lower extent. The direct inputs are associated mainly with the manufacture and use of its ammonium salt, with minimal contributions from other PFOA salts (potassium, sodium and silver salts (van der Putte et al., 2009). The indirect inputs are as an unintended by-product in products containing fluoropolymer and/or fluorotelomer-based materials (van der Putte et al., 2009).

PFOA concentrations continued to rise in gannet eggs for another 4 years after PFOS levels started to decline. This is most likely linked to differences in the timing of implementation of regulatory control measures. While the voluntary withdrawal of PFOS began in the early 2000s, the phase out of PFOA began only in 2006 (Groffen et al., 2017) following agreement by major US companies, to decrease the emissions and the contents of products in PFOA, higher homologues, and precursors by 95% by 2010. PFOA concentrations in AC gannet eggs had already started to decline by the mid-2000s (Fig. 5), suggesting emissions into Irish Sea ecosystems were already on the wane. This is consistent with results obtained in white-tailed eagle (*Haliaeetus albicilla*) feathers from Greenland (Sun et al., 2019). It is unclear to what extent PFOA concentrations in BR gannet eggs may have declined over the same period, partly because the variability in PFOA concentrations was high in eggs collected in 2014 together with the limited number of measurements from when the levels started to decline (Fig. 5). It is possible that inputs or bioaccumulation of PFOA into the North Sea food-chains may have reduced at a slower rate than in the Irish Sea food-chains. Similarly, contrasting temporal trends between these colonies were also observed for some PCB congeners (Pereira et al., 2009), suggesting that inter-colony variations occur for a wide range of contaminants. It was only in 2019 that the United Nations agreed a global ban on the use of PFOA, its salts and related compounds (with some exemptions) and they were added to Annex A of the Stockholm Convention (Chemical Watch, 2019).

4.3. Toxicity

There are limited embryotoxicity data for fluorinated compounds in birds. Most data relate to PFOS, albeit in a limited number of species, and observed effects include increased liver weight in mallards (*Anas platyrhynchos*), pathological liver changes in northern bobwhite quail (*Colinus virginianus*) and white leghorn chicken (*Gallus domesticus;* Gallagher et al., 2003; Molina et al., 2006), increased fatty acid oxidation (Nordén et al., 2012) and hypothyroidism (McNabb et al., 2005) in bobwhites and various immunological, morphological, and neurological effects (Peden-Adams et al., 2009). Newsted et al. (2007) suggested a Predicted No Effect Concentration (PNEC) of 1 μg/ml egg yolk for PFOS in eggs, based on reproductive effects in bobwhite quail, equivalent to 29 ng g^{-1} in a whole egg, assuming that an egg is 29% yolk/71% albumen *w*/w, as measured in herring gull (*Larus argentatus)* eggs (Gebbink and Letcher, 2010), and that the yolk has 1.0 g/ml specific gravity.

Furthermore, a Lowest-Observable-Adverse-Effect (LOAEL) for PFOS in eggs, based on reduced hatchability in white leghorn chickens, has been reported as 100 ng g^{-1} (Molina et al., 2006).

In the gannets analysed in this study, the majority of eggs in both colonies contained PFOS residues above the PNEC (76% of eggs in AC and 91% in BR) while 9% of AC eggs between 1994 and 2002 and 14% of BR eggs between 1990 and 2002 exceed the LOAEL. This suggests that although PFAS concentrations overall in gannets were relatively low, the observed levels of PFOS alone may have affected some eggs hatchability. Furthermore, the gannet eggs also contained PFCAs and their potential toxic effects are less well known than those of PFOS. Tartu et al. (2014) studied the effects of long-chained PFCAs in black-legged kittiwakes (*Rissa tridactyla*) and found negative associations between: a) PFNA and male body condition; b) PFDoA and reduced hatching success and c) PFTriDA and PFTeDA decreased glucocorticoid hormones. Therefore, the embryotoxicity resultant from exposure to fluorinated compounds will only be fully understood when more is known on the effects off individual and mixtures of these compounds in a range of bird species.

5. Conclusions

This study investigated the concentrations of perfluorinated compounds in gannet eggs, a marine environmental sentinel, from a North Sea and an Irish Sea (Eastern Atlantic) colony. PFAS profiles remain dominated by PFOS, although our long-term analysis demonstrated that concentrations of PFOS, and that of PFOA, have largely declined. This indicates that restrictions and then bans on use have been effective, although the extent of any decline in PFOA in eggs from the North Sea colony were uncertain. Temporal trends in other PFCAs, specifically long-chain odd compounds, contrasted with that for PFOA in that they have increased by ~10 fold in the last 30 years and the rise appears ongoing.

In the first 20 years, PFSAs accounted for >90% ΣPFAS in eggs but from 1994 onwards the proportion decreased to between 62% and 73%, suggesting a temporal decline of PFSAs combined with increase of PFCAs.

The availability of toxicity data for many PFAS alone, and in combination with each other, is limited. This knowledge gap, coupled with our detection of multiple PFAS in eggs and a trend of rising concentrations in some PFCAs, including longer-chain compounds that are more toxic and bioaccumulative than shorter-chain ones, means that PFAS remain an environmental concern, and could be causing long term damage to top predators and human life. Better understanding of continuing tends in exposure and the toxicity of those compounds that are rising in concentrations, is needed in order to assess the current and future risk of PFAS to marine top predators.

CRediT authorship contribution statement

M. Glória Pereira- responsible for the overaching research goals, data analyses and writting of the manuscript and

Silvia Lacorte- responsible for the chemical analyses and comments on the manuscript pre-publication

Lee A. Walker- Coordination of sample collection and preparation.

Richard F. Shore- Management, oversight and leadership responsibility for the PBMS project. Critical review of the manuscript pre-publication.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.141900.

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