Perfluorinated compound (PFC) concentrations in northern gannet eggs 1977-2014: a Predatory Bird Monitoring Scheme (PBMS) report

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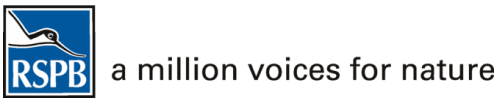

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Contents

1 Executive Summary

The Predatory Bird Monitoring Scheme (PBMS; http://pbms.ceh.ac.uk/) is the umbrella project that encompasses the Centre for Ecology & Hydrology's National Capability activities for contaminant monitoring and surveillance work on avian predators. The PBMS aims to detect and quantify current and emerging chemical threats to the environment and in particular to vertebrate wildlife.

Perfluorinated compounds (PFCs) are a class of compounds that are used worldwide as surface treatments on textiles, leather and carpet, in paper products used for food preparation and storage, and in firefighting foams, insecticides and floor polishes (Custer et al., 2012). PFCs consist of a hydrocarbon chains where the hydrogen atoms have been substituted by a fluorine atom. Commonly a functional group, such as a carboxylate or sulfonate, is added to one of the carbons in the chain. The length (number of carbon atoms) in the chain and the type and position of the functional group determine the physiochemical properties of the individual compound and consequently its use and environmental fate and toxicity.

This report presents the results of a study to quantify the concentrations of perfluorinated compounds (PFCs) in the eggs of the northern gannet, *Morus bassanus*, a sentinel for marine contamination. Eggs were collected from the Ailsa Craig (Irish Sea/eastern Atlantic) and Bass Rock (North Sea) colonies off the UK coast collected between 1977 and 2014 and analysed for a range of PFCs. The principle aims of this work were to determine the concentrations of PFCs accumulated in the eggs of gannets, whether they had changed over the monitoring period, whether contamination varied between colonies, and how concentrations compared with those associated with adverse effects.

The egg contents were analysed by Liquid Chromatograph – Mass Spectrometry (LC-MS) techniques. Compounds from both the perfluorinated carboxylate and perfluorinated sulfonate groups of PFCs were quantified.

Overall temporal trends in PFC concentrations differed for sulfonates and carboxylates. Egg concentrations of sum sulfonated PFCs, overwhelmingly comprised of perfluorooctane sulfonic acid (PFOS), increased up until 1995 but then declined whereas concentrations of sum carboxylated PFCs have increased in a broadly linear fashion since the mid-1980s and appear to be continuing to do so.

Sum sulfonate concentrations in eggs did not differ between colonies but sum carboxylate PFC concentrations, and concentrations of the individual carboxylates, perfluorododecanoic acid (PFDoA) and perfluorotridecanoic acid (PFTriDA), were significantly higher in eggs from Ailsa Craig than those from Bass Rock over the monitoring period as a whole

PFC concentrations were lower than those in eggs of other bird species from sites with local PFC sources but similar to concentrations in gull eggs from the Arctic and Iceland. The mean concentrations of PFOS in gannet eggs from both Ailsa Craig and Bass Rock were between the predicted no effect concentration (PNEC) and lowest observed adverse effect concentration (LOAEL) previously reported for the eggs of other species.

2 Introduction

2.1 Background

The Predatory Bird Monitoring Scheme (PBMS; http://pbms.ceh.ac.uk/) is the umbrella project that encompasses the Centre for Ecology & Hydrology's long-term contaminant monitoring and surveillance work on avian predators. The PBMS is a component of CEH's National Capability activities but elements of the project are also funded by a range of other stakeholders (see Section 6).

By monitoring sentinel vertebrate species, the PBMS aims to detect and quantify current and emerging chemical threats to the environment and, in particular, to vertebrate wildlife. Our monitoring provides scientific evidence of how chemical risk varies over time and space. This may occur due to market-led or regulatory changes in chemical use and may also be associated with larger-scale phenomena, such as global environmental change. Our monitoring also allows us to assess whether detected contaminants are likely to be associated with adverse effects on individuals and their populations.

Overall, the PBMS has two key general objectives:

(i) to detect temporal and spatial variation in exposure, assimilation and risk for selected pesticides and pollutants of current concern in sentinel UK predatory bird species and in species of high conservation value

(ii) in conjunction with allied studies, to elucidate the fundamental processes and factors that govern food-chain transfer and assimilation of contaminants by top predators.

Further details about the PBMS, copies of previous reports, and copies of (or links to) published scientific papers based on the work of the PBMS can be found on the PBMS website.

The wider impact of the PBMS is that it provides a scientific evidence base to inform regulatory and policy decisions about sustainable use of chemicals. The outcomes of PBMS monitoring are used to assess whether effects are likely to occur in wildlife, whether mitigation of exposure is needed and what measures might be effective. Monitoring also provides information by which the success of mitigation measures can be evaluated.

One key policy area particularly relevant to the current report, is how data collected by the PBMS provides evidence for the impacts of the Stockholm Convention, a global treaty to protect human health and the environment from persistent, organic pollutants (POPs). The Convention was adopted in 2001 and entered into force in 2004. It requires its parties, which include the UK, to take measures to eliminate or reduce the release of POPs into the environment. The monitoring studies of the PBMS, in tracking spatial and temporal trends of POPs in sentinel predatory and fish eating birds, provides evidence of the effectiveness of the Convention.

2.2 Perfluorinated compounds

Perfluorinated compounds (PFCs) are a class of compounds used worldwide as surface treatments on textiles, leather and carpet, in paper products used for food preparation and storage, and in firefighting foams, insecticides and floor polishes (Custer *et al.*, 2012). PFCs consist of hydrocarbon chains where the hydrogen atoms have been substituted by fluorine. Commonly it is a functional group, such as a carboxylate or sulfonate, that is added to one of the carbons in the chain and so most PFCs are separated into perfluoroalkylcarboxylic acids (carboxylates) and perfluoroalkylsulfonates (sulfonates; Table 1). The length (number of carbon atoms) in the chain and the type and position of the functional group determine the physiochemical properties of the individual compound and consequently its use and environmental fate and toxicity.

Increasing production over previous decades has led to increasing exposure of birds and fish species to these compounds (Gebbink and Letcher, 2012). Other factors, such as proximity to sources, have can influence the concentrations of these compounds in wildlife (Gebbink et al., 2009). Long-chain perfluorinated chemicals (C9-C13) are bioaccumulative in wildlife and humans, and are persistent in the environment. To date, significant adverse effects have not been found in the general human population but adverse effects, associated with exposures in the parts per million range, have been identified in laboratory animals and wildlife (USEPA, 2009). Perfluorooctane sulfonate (PFOS) has been shown to cause reduced hatchability and chick survival in birds, reduced cumulative fecundity and fertility in fish and delays in growth and metamorphosis in amphibians.

The use of one prevalent PFC, PFOS, is restricted due to its inclusion in Annex B of the Stockholm Convention and is subject to action plans aimed at reducing the environmental impact of PFOS, and it's precursors, both in the USA and the United Kingdom (Footitt *et al.*, 2004, USEPA, 2009).

The PBMS collects analyses and archives the eggs of the northern gannet, *Morus bassanus*, as part of its long term monitoring activities. This species acts as a sentinel for changes in marine pollution. Eggs are collected in alternate years from two gannet colonies (Figure 1), Ailsa Craig (off the south west coast of Scotland) and Bass Rock (North Sea). Both colonies are comprised of between 30,000 and 35,000 breeding pairs which combined equates to approximately 16% of the world population of this species. As a top predator, gannets are likely to be exposed to those chemical contaminants that biomagnify through the marine food chain due to their persistence and bioaccumulative properties.

This study quantified the concentrations of PFCs in gannet eggs collected from the Ailsa Craig and Bass Rock colonies between 1977 and 2014. The principle aim was to determine the concentrations of PFCs accumulated in eggs, whether these changed over the course of the monitoring period, if they varied between colonies, and whether the concentrations that were accumulated were likely to be associated with adverse effects.

Table 1. Identity of Perfluorinated Compounds (PFCs)

Acronym	Name	Formula	CAS Number	Type	Analysed in the current study
PFBA	Perfluorobutanoic acid	C_3F_7COOH	375-22-4	Carboxylate	Yes
PFPA	Perfluoropentanoic acid	C_4F_9COOH	2706-90-3	Carboxylate	No
PFHxA	Perfluorohexanoic acid	$C_5F_{11}COOH$	307-24-4	Carboxylate	No
PFHpA	Perfluoroheptanoic acid	$C_6F_{13}COOH$	375-85-9	Carboxylate	No
PFOA	Perfluorooctanoic acid	$C_7F_{15}COOH$	335-67-1	Carboxylate	Yes
PFNA	Perfluorononanoic acid	$C_8F_{17}COOH$	375-95-1	Carboxylate	Yes
PFDA	Perfluorodecanoic acid	$C_9F_{19}COOH$	335-76-2	Carboxylate	Yes
PFUnA	Perfluoroundecanoic acid	$C_{10}F_{21}COOH$	4234-23-5	Carboxylate	Yes
PFDoA	Perfluorododecanoic acid	$C_{11}F_{23}COOH$	307-55-1	Carboxylate	Yes
PFTriDA	Perfluorotridecanoic acid	$C_{15}F_{25}COOH$	72629-94-8	Carboxylate	Yes
PFTeDA	Perfluorotetradecanoic acid	$C_{13}F_{27}COOH$	376-06-7	Carboxylate	Yes
PFHxDA	Perfluorohexadecanoic acid	$C_{15}F_{31}COOH$	67905-19-5	Carboxylate	No
PFBS	Perfluorobutane sulfonate	$C_4F_9SO_2O$-	29420-49-3[1]	Sulfonate	No
PFHxS	Perfluorohexane sulfonate	$C_6F_{13}SO_2O$-	3871-99-6[1]	Sulfonate	Yes
PFHpS	Perfluoroheptane sulfonate	$C_7F_{15}SO_2O$-	-	Sulfonate	No
PFOS	Perfluorooctane sulfonate	$C_8F_{17}SO_2O$-	1763-23-1[2]	Sulfonate	Yes
PFDS	Perfluoro-1-decanesulfonate	$C_{10}F_{21}SO_2O$-	13419-61-9[2]	Sulfonate	Yes
THPFOS (6:2 FTS)	1H,1H,2H,2H-perfluorooctane sulfonate	$C_6F_{13}C_2H_4SO_3^-$	27619-97-2	Sulfonate	No
PFOSi	Perfluorooctane sulfinate	$C_8F_{17}SO_2^-$	-	Sulfonate	No
PFOSA	Perfluorooctane sulfonamide	$C_8F_{17}SO_2NH_2$	754-91-6	Sulfonate	No

[1] CAS number given is for potassium salt, [2] CAS number given is for sodium salt.

3 Methods

3.1 Collection of eggs

The eggs used in this study were collected under licence as part of the long-term monitoring programme of the Predatory Bird Monitoring Scheme. Ten fresh eggs were taken during laying or the early incubation period from separate nests from the Ailsa Craig and Bass Rock colonies. The length, breadth and weight of each egg were measured and contents were collected by cracking the eggs open. The contents were homogenized and kept at -20ºC prior to this analysis.

For this study a sub-set of 4-6 eggs were randomly selected from those collected in each of the years that were chosen for analysis over the period 1977 to 2014 (Table 2). In total, 57 eggs from Bass Rock and 54 eggs from Ailsa Craig were analysed.

Figure 1. Location of Ailsa Craig (West Scotland) and Bass Rock (East Scotland).

Table 2. Summary of number of northern gannet eggs analysed for perfluorinated compounds for each year included in the study.

Year	No/ eggs analysed		Year	No/ eggs analysed	
	Bass rock	Ailsa Craig		Bass rock	Ailsa Craig
1977	5	4	1998	6	5
1981	5	4	2002	5	6
1985	5	5	2006	6	-
1987	5	5	2007	-	5
1990	5	5	2013	-	5
1992	5	5	2014	5	-
1994	5	5	Total	57	54

3.2 Analytical methods

PFCs were solid-liquid extracted from homogenized wet samples using acetonitrile. One g of eggs was weighed in polypropylene tubes and internal standards (m-PFOS and m-PFOA) were added at a concentration of 100 ng/g, and incubated for 18 hours at 4ºC. Nine millilitres (mls) of acetonitrile were added and the samples were thoroughly mixed using a vortex mixer. Samples were extracted in an ultrasonic bath for 10 min at room temperature. This procedure (vortexing and ultrasonic extraction) was repeated 3 times without changing the solvent.

The samples were then centrifuged at 2,500 rpm for 5 minutes. The supernatant was transferred to a new vial and evaporated to dryness. Then, 1 ml of acetonitrile was added to the dried sample and incubated for 10 min in the ultrasonic bath. The samples were purified by adding 25 mg of activated carbon and 50 µL of glacial acetic acid and were vigorously mixed for 1 minute. Afterwards, the samples were centrifuged for 10 min at 10,000 rpm. The supernatant was transferred to a clean micro-vial, and 250 µl of this were diluted with 250 µl of 10 mM ammonium acetate buffer of mobile phase. PFCs were measured using an Acquity Ultra Performance Liquid Chromatography system connected to a Triple Quadruple Mass Spectrometry Detector (Waters, USA) with an Acquity UPLC BEH C18 column (1.7 µm particle size, 100 mm x 2.1 mm, Waters, USA) using MRM. Five µl of extract were injected. Internal standard quantification was performed using m-PFOS to quantify PFHxS, PFOS and PFDS and m-PFOA to quantify PFBA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTriDA and PFTeDA (see Table 1 for details of individual analytes).

A mixture of native perfluoroalkylcarboxylic acids and native perfluoroalkylsulfonates was supplied by Wellington Laboratories (Ontario, Canada). Stock standard solutions were prepared in acetonitrile at a concentration of 5 ng/µl for all native compounds and were stored at -18ºC. Perfluoro-n-(1,2,3,4-13C4) octanoic acid (m-PFOA) and sodium perfluoro-1-(1,2,3,4-13C4) octanesulfonate (m-PFOS), also from Wellington Laboratories, were used as surrogate standards for the carboxylates and sulfonates, respectively. HPLC grade water and acetonitrile were supplied by Merck (Darmstadt, Germany) and glacial acetic acid from Panreac (Barcelona, Spain). Average recoveries for internal PFC recovery standards ranged between 72% and 144%. The mean method limit of detection (LoD) for the carboxylate PFCs was 0.060 ng $g^{-1}$and ranged from 0.015 to 0.107 ng g^{-1}, while the LoD for the sulfonate PFCs was 0.028, 0.084 and 0.137 ng g^{-1} for PFDS, PFHxS and PFOS, respectively.

3.3 Data expression, format and analysis

Throughout this report, egg concentrations of perfluorinated compounds are reported as ng/g wet weight (wet wt). A correction factor was applied for desiccation by multiplying concentrations by the total egg weight/volume ratio. Egg volume was estimated using the equation $V = 0.51 \times LB^2$, where L is egg length and B is egg breadth (Hoyt, 1979).

When summed PFC concentrations were calculated, individual compound concentrations below the limit of detection (non-detected) were assigned a zero value.

General linear models and non-linear fitted line plots (quadratic relationships) were performed using Mintab version 16.1 (Minitab Ltd., U.K.), while all other statistical tests and graphing of results were performed using GraphPAD Prism version 5.00 for Windows (GraphPad Software, San Diego California USA, www.graphpad.com).

4 Results and Discussion

4.1 Perfluorinated compounds in northern gannet eggs

PFCs were detected in all the eggs analysed. When carboxylates and sulfonates were considered separately, individual sum concentrations ranged from 1.61 to 34.5 ng g^{-1} wet wt. and 16.5 to 165 ng g^{-1} wet wt., respectively. The composition of the carboxylates and sulfonates (proportion of each compound contributing to the sum concentrations) were similar for the two colonies (Figure 2). Perfluorooctane sulfonate (PFOS) was by far the predominant sulfonate, always accounting for 97-99% of sum sulfonate concentrations in eggs and perfluorotridecanoate (PFTriDA) and perfluoroundecanoate (PFUnA) were the most prevalent carboxylates, comprising on average 59% and 22% respectively of the sum carboxylate concentration over the duration of the monitoring period.

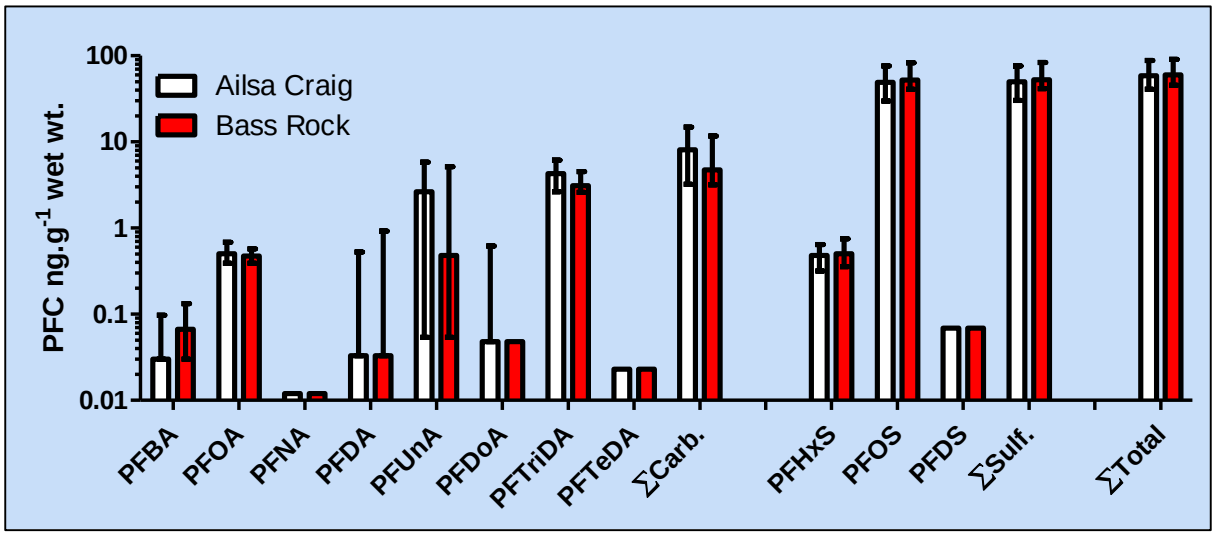

Figure 2. Median (± Inter-Quartile Range) concentrations of perfluorinated compounds in gannet eggs from Alisa Craig and Bass Rock colonies collected between 1977 and 2014. Note that y-axis is on a logarithmic scale and sum carboxylate PFCs (∑Carb.), sum sulfonate PFCs (∑Sulf.) and sum PFCs (∑Total) compounds are also shown.

4.2 Time trends in PFC concentrations

Sum concentrations of all PFCs combined appeared to increase over the initial part of the monitoring period but peak in approximately the mid-1990s (Figure 3). Initial data exploration suggested that time trends differed for carboxylates and sulfonates and thus complicated analysis of time trends for PFCs overall. Further analysis was conducted separately on the two groups.

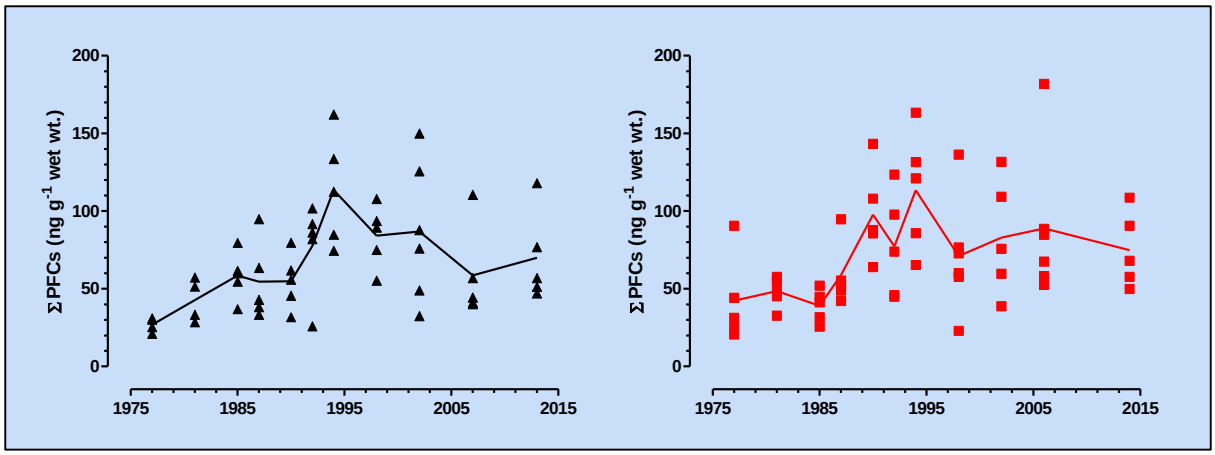

Figure 3. Sum concentrations PFCs in gannet eggs from Ailsa Craig (▲) and Bass Rock (■) colonies. Trends on are shown by the connecting line that joins annual arithmetic mean concentrations.

Time trends in sum sulfonate concentrations in eggs from Ailsa Craig were significantly explained by a quadratic non-linear relationship (R^2 = 0.254, $F_{2,51}$ = 8.69, P=0.001; Figure 4) with concentrations rising until approximately 1995 and then declining. There was a similar temporal trend in eggs from Bass Rock (Figure 4) although it was not possible to describe this statistically (because of non-normality of residuals in the analysis). Paired comparison of annual arithmetic mean sulfonate concentrations by year indicated that there was no significant difference between colonies (t_{10}=1.469, P=0.18).

Initial inspection of the data for carboxylate concentrations (not logged) indicated that concentrations were largely undetectable until 1987 and then started to increase. This increase was statistically significant (Generalized Linear Model: effect of year: $F_{7,67}$ = 13.4, P<0.001; Figure 4) and was similar between colonies but concentrations were consistently higher in eggs from Ailsa Craig (Generalized Linear Model: effect of colony: $F_{1,67}$ = 8.94, P=0.004).

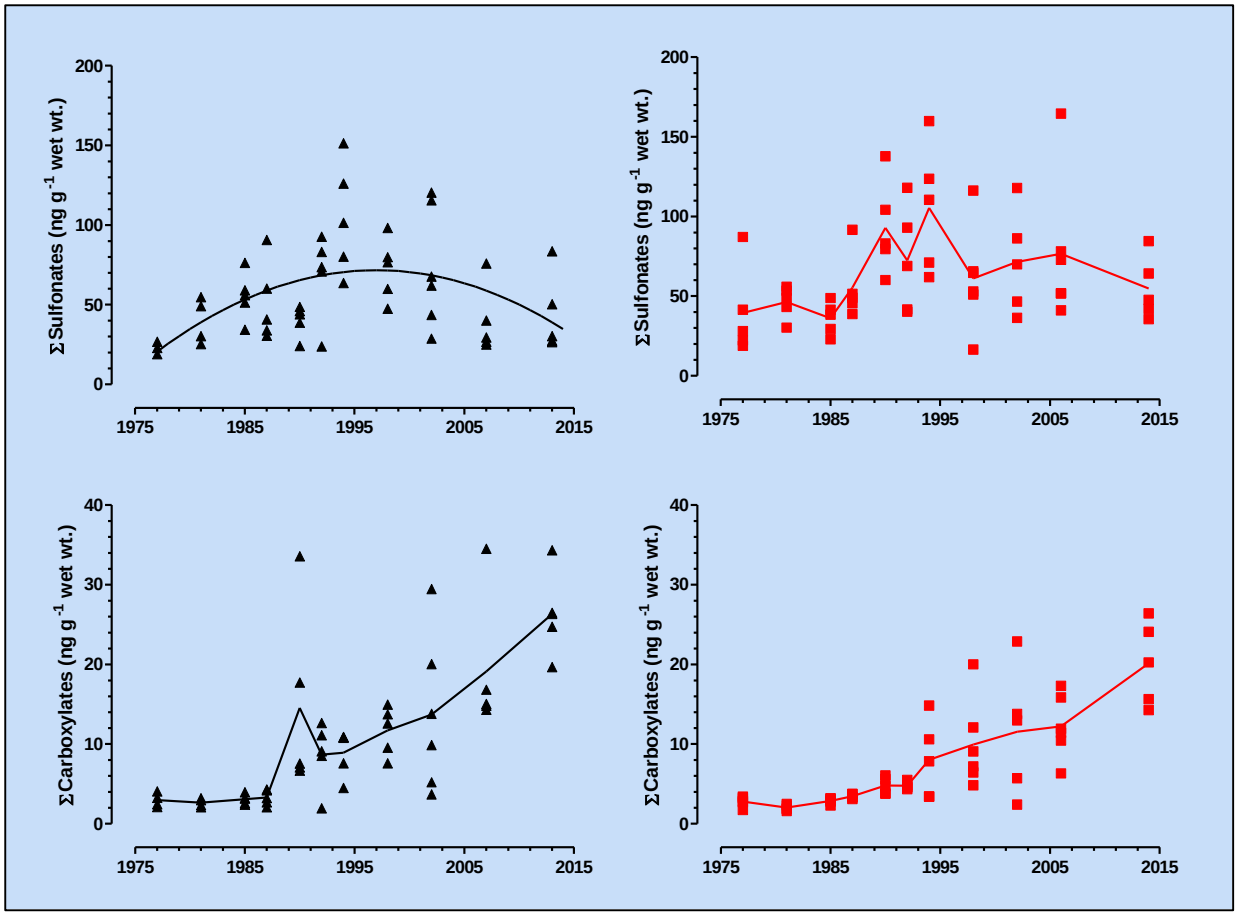

Figure 4. Sum concentrations of sulfonate and carboxylate PFCs in gannet eggs from Ailsa Craig (▲) and Bass Rock (■) colonies. Quadratic regression line shown for sum sulfonate PFCs in Ailsa Craig eggs (∑Sulfonates=15.4+5.356*X-0.1275*X^2; where X=Year - 1976). Trends on other graphs are shown by the connecting line that joins annual arithmetic mean concentrations.

When individual sulfonates were considered, the sulfonate profile was overwhelmingly dominated by PFOS and the time trends for PFOS were identical to those of the sum sulfonates. PFHxS was the only other sulfonate detected in most eggs throughout the monitoring period (PFDS was detected in only a small number of eggs — data not shown). The temporal pattern for PFHxS in eggs from Ailsa Craig was similar to that for PFOS, with a rise in concentrations to the mid to late 1990s followed by a decline in concentrations (R^2 = 0.270, $F_{2,51}$ = 9.43, P<0.001; Figure 5). PFHxS concentrations in eggs from Bass Rock likewise appeared to increase until approximately the year 2000, and then start to decline (Figure 5), but the quadratic regression was not statistically significant (R^2 = 0.096, $F_{2,51}$ = 2.70, P=0.077). There was no significant difference between colonies in annual arithmetic mean PFHxS concentrations (Paired t-test: t_{10}=1.143, P=0.280).

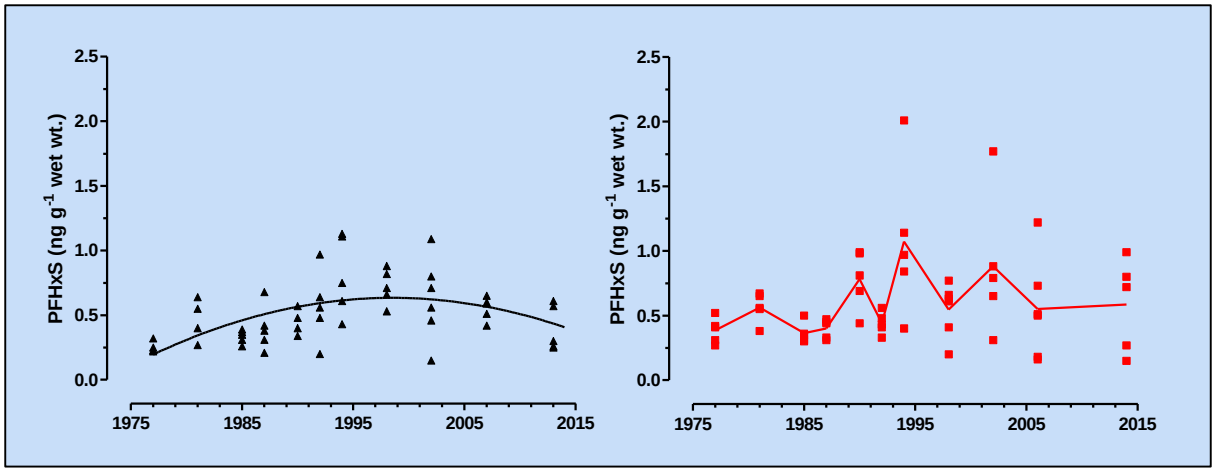

Figure 5. Concentrations of PFHxS in gannet eggs from Ailsa Craig (left-hand graph) and Bass Rock (right-hand graph). Quadratic regression line shown for eggs from Ailsa Craig (PFHxS=0.153+0.043*X-0.001*X2; where X=Year-1976). Trends on other graph is shown by the connecting line that joins annual arithmetic mean concentrations.

PFUnA, PFTriDA, PFNA, PFDA and PFDoA were the predominant carboxylates and generally followed the same temporal profile as that for the summed carboxylates, with an increase in concentrations in later years, except perhaps for PFTriDA for which the annual increase appeared to be more consistent throughout the monitoring period (Figure 6). Temporal patterns were not apparent in the remaining carboxylates which we measured (PFBA, PFOA and PFTeDA); they were present in lower amounts or were often non-detectable (Figure 6). Paired t-tests, paired on the basis of collection year indicated that annual arithmetic mean concentrations of PFTriDA (t_{10}=3.346, P=0.007) and PFDoA (t_{10}=2.383, P=0.038) were significantly higher in eggs from Ailsa Craig than those from Bass Rock.

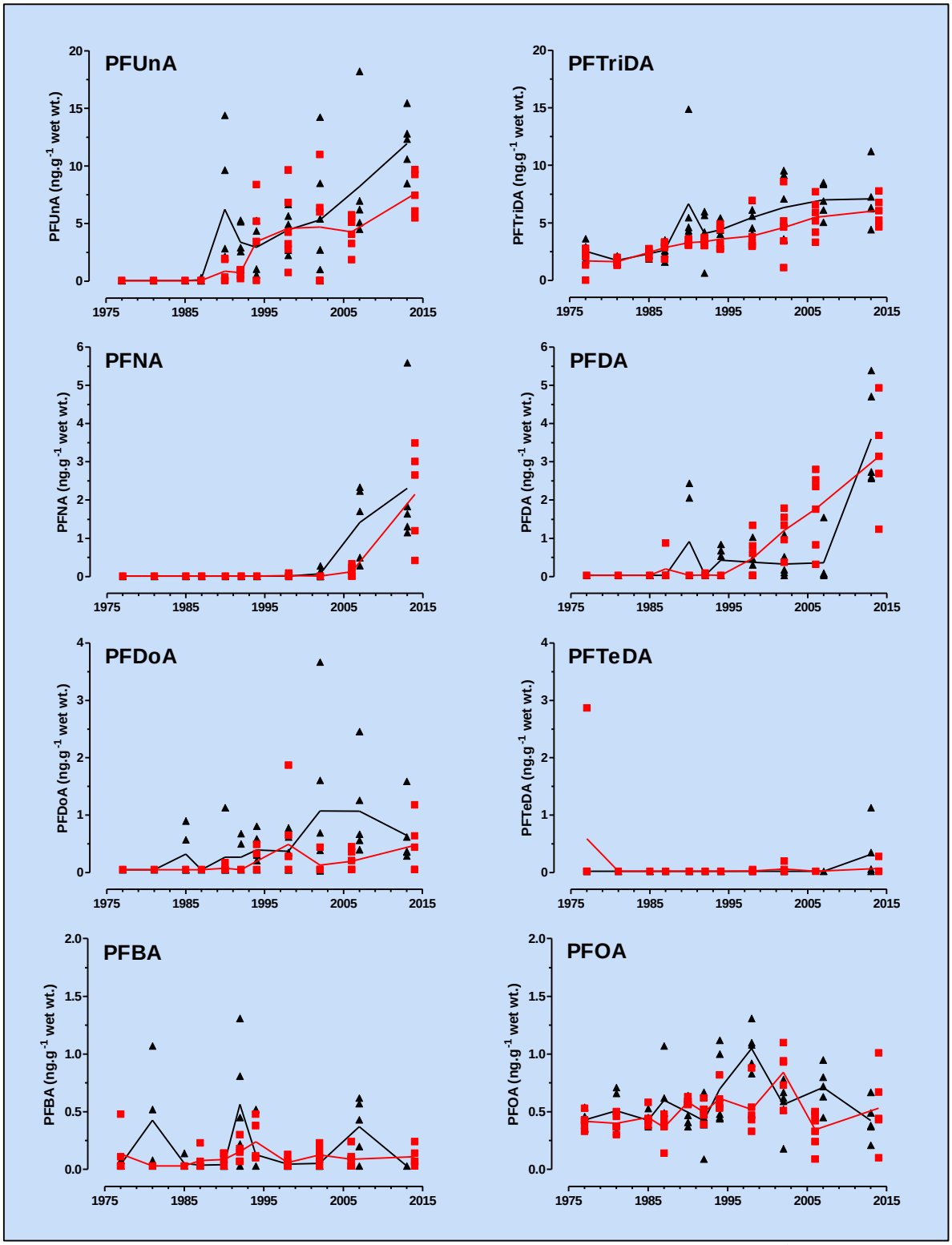

Figure 6. Concentrations of carboxylate perfluorinated compounds (ng g^{-1} wet weight) in individual gannet eggs from Ailsa Craig (▲) and Bass Rock (■) colonies. Connecting line indicates mean concentration for each sampling year.

4.3 How do our findings compare to other studies and with adverse effects?

As the suite of PFC compound quantified varies among studies, it is only generally valid to compare concentrations of individual compounds rather than sum PFC residues. Concentrations of the predominant PFC compound, PFOS, in eggs from Ailsa Craig and Bass Rock were lower than the highest previously reported average concentrations (1253 ng g^{-1} wet wt.) measured between 2006 and 2009 in double-crested cormorants, *Phalacrocorax auritus*, from the heavily urbanised estuary of San Francisco Bay (Sedlak and Greig, 2012). Overall, the average concentrations of PFOS measured in our study are in the lowest third of those previously reported in studies that encompass 10 species from 20 sites from North America, the Artic, Europe, and southern China. Similar concentrations (range of averages 46-84 ng g^{-1} wet wt.) to those in gannets in the present study have been reported for gull species from the Artic, Iceland and reference sites in the Great Lakes (Gebbink and Letcher, 2010, Giesy and Kannan, 2001, Holström and Berger, 2008, Holström *et al.*, 2005, Miljeteig *et al.*, 2009).

Holström & Berger (2008) demonstrated an increase in PFOS in guillemot eggs, *Uria aalge*, between 1968 and 2003 to a maximum level of 1324 ng g^{-1} wet wt. in 1997 (pooled sample of 8 eggs); by 2003 the concentration had fallen to 614 (range 551-669; mean of 9 eggs). PFOS concentrations in gannet eggs in the present study followed a similar temporal pattern but the magnitude of residues were lower than in the guillemots. The gannet eggs also had relatively low concentrations of PFNA, PFDA, PFDoA compared to other studies while concentrations of PFOA, PFUnA and PFHxS were within the inter-quartile range of the median concentrations reported in other studies.

Embryotoxicity data for PFCs in birds is limited and appears to be restricted largely to PFOS. Newstead et al (2005) suggests a predicted no effect concentration (PNEC) for PFOS in eggs, based on reproductive effects in dietary exposed northern bobwhite quail, *Colinus virginianus*, of 1µg ml^{-1} egg yolk. This PNEC would be equivalent to a whole egg concentration of 29 ng g^{-1} assuming a yolk specific gravity of 1.0 g ml^{-1} and after adjusting concentrations in yolk to concentrations in the whole eggs using a 29% yolk to 71% albumen mass ratio measured in Norwegian herring gull, *Larus argentatus*, eggs (Gebbink and Letcher, 2010). The majority of eggs (both colonies, most years) contained PFOS residues that exceeded this PNEC value. However, PFOS concentrations in gannet eggs were lower than egg concentrations that were associated with adverse effects in other species. PFOS-mediated effects on hatching and pipping success in domestic chickens eggs were associated with doses (injected into the air space of the egg) ranging from 0.1 µg g^{-1} egg (lowest observed adverse effect level, LOAEL) to 100 µg g^{-1} (Molina et al., 2006, O'Brien et al., 2009). The lower of these PFOS concentrations was exceeded in individual gannet eggs from both Bass Rock (years 1992 to 2006) and Ailsa Craig (years 1994 and 2002), while the majority of eggs from both colonies were within an order of magnitude of this 0.1 µg g^{-1} concentration.

Overall our data suggests that gannet eggs from both Ailsa Craig and Bass Rock contained lower PFC concentrations compared to bird eggs taken from sites with local sources of contamination but concentrations were similar to those in eggs of gull species from the Artic and Iceland. Concentrations of PFOS in the gannet eggs were between the PNEC and LOAEL values previously reported in bird eggs. While sulfonate residues in gannet eggs appear to have peaked in the mid-1990s, sum carboxylate concentrations have increased steadily by approximately 10 fold in the last 30 years and this increase appears to be ongoing.

5 Acknowledgements

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