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Effects of environmental exposure and diet on levels of persistent organic pollutants (POPs) in eggs of a top predator in the North Atlantic in 1980 and 2008

Eliza H.K. Leat [a], Sophie Bourgeon [b], Katrine Borgå [c], Hallvard Strøm [d], Sveinn A. Hanssen [b], Geir W. Gabrielsen [d], Ævar Petersen [e], Kristin Olafsdottir [f], Ellen Magnusdottir [f], Aaron T. Fisk [g], Sandra Ellis [g], Jan O. Bustnes [b], Robert W. Furness [a,*]

[a] College of Medical, Veterinary and Life Sciences, Graham Kerr Building, University of Glasgow, Glasgow G12 8QQ, UK
[b] Norwegian Institute for Nature Research, FRAM Centre, 9296 Tromsø, Norway
[c] Norwegian Institute for Water Research, Gaustadalleén 21, 0349 Oslo, Norway
[d] Norwegian Polar Institute, FRAM Centre, 9296 Tromsø, Norway
[e] Icelandic Institute of Natural History, IS-105 Reykjavik, Iceland
[f] University of Iceland, Department of Pharmacology & Toxicology, IS-107 Reykjavik, Iceland
[g] Great Lakes Institute of Environmental Research, University of Windsor, Windsor, Ontario, N9B 3P4, Canada

Great skua eggs from Shetland show a decrease in legacy POPs and an increase in PBDEs between 1980 and 2008, and an influence of diet composition.

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ABSTRACT

Concentrations of POPs in Great skua eggs from Shetland are among the highest in North Atlantic seabirds, with up to 11,600 μg/kg (ww) DDE and up to 17,900 μg/kg ww ∑PCB. Concentrations of legacy POPs were significantly lower in 2008 than 1980. Decreases were greatest for least persistent compounds. Median ∑PBDEs increased from 99 μg/kg ww in 1980 to 173 μg/kg ww in 2008. There were changes in Great skua breeding season diet, with more adult Herring and Mackerel and less Sandeel. These changes increase exposure to POPs, since Herring and Mackerel accumulate more POPs than Sandeels. In both years, eggs with higher $\delta^{15}N$ had higher POP concentrations. In 1980, birds feeding more on demersal discard fish from trawl fisheries and less on Sandeels, had higher POP levels in eggs. In 2008, individuals feeding more on Herring and Mackerel, and less on discards, had higher POP levels in eggs.

1. Introduction

Persistent organic pollutants (POPs) include "legacy" POPs such as dichlorodiphenyldichloroethylene (DDE) and polychlorinated biphenyls (PCBs), and "new" POPs such as brominated flame retardants (mainly polybrominated diphenyl ethers, PBDEs) (Lavoie et al., 2010; Lindström et al., 1999; Muir and de Wit, 2010). POPs that are released into the environment, being volatile in warm climates, can be transported over large distances via atmospheric circulation, before being deposited in colder environments (Muir and de Wit, 2010). Most POPs are hydrophobic and persistent in the environment; as a result, they tend to bioaccumulate in organisms (Newman, 2010). POPs biomagnify in food webs, so reach highest concentrations in top predators (Fisk et al., 2001; Gabrielsen, 2007). Since POPs are toxic at high exposures, there is concern not only about hazards to human health through contaminated seafoods (Food Standards Agency, 2006), but also about possible toxic effects of POPs on top predators (Muir and de Wit, 2010; Letcher et al., 2010).

Seabird eggs have frequently been used to monitor trends in levels of POPs in marine ecosystems (Braune, 2007; Helgason et al., 2008, 2010; Jörundsdóttir et al., 2010; Lavoie et al., 2010; Pereira et al., 2009). Hydrophobic/lipophilic compounds are transferred along with fat from the female into developing eggs. At least within species, concentrations in eggs reflect the contaminant burden of the female at the time of laying, especially the uptake of contaminants from food recently ingested around the colony although some contaminants may derive from accumulation in winter quarters mobilized from adipose tissue (Becker et al., 2001; Braune and Norstrom, 1989; Verreault et al., 2006). Restrictions, or bans, on the use of organochlorine insecticides and PCBs in Europe and North America since the 1970s have resulted in large decreases in levels of legacy POPs in

* Corresponding author.
E-mail address: bob.furness@glasgow.ac.uk (R.W. Furness).

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terrestrial ecosystems (Lead et al., 1997; Verreault et al., 2010). A reduction has also been apparent in eggs of some seabirds in some ecosystems (Braune, 2007; Helgason et al., 2008; Pereira et al., 2009). However, despite the restricted use of legacy POPs, levels in seabird eggs in some cases have shown little or no decrease or have continued to increase (Helgason et al., 2010). For example, concentrations of certain PCB congeners continued to increase in Northern gannet *Morus bassanus* eggs from the Bass Rock, east Scotland from 1990 to 2004 (Pereira et al., 2009). Much of the emphasis on monitoring trends in legacy POPs has focused on Arctic marine ecosystems, while few data are available from lower latitudes. In the context of the marine ecosystem around the British Isles, Pereira et al. (2009) concluded "the lack of any decline in some contaminants, for example some of the heavier PCB congeners in gannets at Bass Rock, highlights a need for further monitoring to determine future risk". In recent decades, additional POPs have also appeared in seabird eggs, such as PBDEs and polychlorinated napthalenes PCNs (Helgason et al., 2009; Bidleman et al., 2010; Lavoie et al., 2010).

Here we present levels of legacy and newer POPs in eggs of a top predator in the Northwest Atlantic, the Great skua *Stercorarius skua*. Based on the literature on long-term trends in POPs in the North Atlantic, we predict that legacy POPs would be higher in Great skua eggs from 1980 and PBDEs would be higher in eggs from 2008. The populations and ecology of this species are well known. About 40% of the world population of the Great skua nests in northern Scotland, and after breeding these birds migrate to winter mostly in the Atlantic off southern Europe and northwest Africa, remaining mostly over the continental shelf area (Furness, 1987). They feed on a wide variety of prey, including fish (both pelagic fish, and scavenged discards from fisheries), other seabirds such as auks, small gulls and petrels, and scavenged items such as Goose-barnacles *Lepas* sp. As top predators they should, therefore, be representative of POP levels in the wider marine ecosystems of the western North Atlantic. Specifically, we compare POP levels in Great skua eggs sampled in 1980 and in 2008 from Shetland, northern Scotland but analysed simultaneously in 2009. The detailed knowledge of Great skua ecology from long-term studies in Shetland (Furness, 1987; Ratcliffe et al., 1998; Votier et al., 2004, 2007, 2008, and references therein) also allows us to relate the measured POP levels to data on the ecology of these birds, including measures of their breeding season diet (pellet composition and stable isotopes of carbon and nitrogen), and breeding performance (egg size, breeding success), in order to assess potential interactions between POP levels in eggs and changing ecological conditions of the population. Changes in diet could particularly influence accumulation of POPs as Great skuas take a wide range of prey. For example, Herring *Clupea harengus* and Mackerel *Scomber scombrus* are longer-lived and larger fish than Sandeels *Ammodytes marinus* and so tend to accumulate higher levels of lipid-soluble contaminants (Food Standards Agency, 2006). Most birds eaten by Great skuas are seabirds, which feed at a higher trophic level than most prey fish (Käkelä et al., 2007), and so likely accumulate higher levels of POPs (Fisk et al., 2001).

2. Materials and methods

2.1. Sample collection

In 1980, 30 eggs were collected under licence, from Great skua nests in Shetland. Shetland is a relatively unpolluted environment, with no major local sources of POPs. Nests were visited daily during the peak period of laying (mid-May) and as soon as the clutch was completed, one of the two eggs was taken at random from each of 30 nests. Eggs were broken in the field, and the contents were transferred into numbered acid-washed glass jars with plastic screw caps. These were then taken to Glasgow University where the contents of each jar were weighed to the nearest 0.1g and then stored at −20 °C until 2008. Sizes of eggs were not measured. In 2008, an additional 30 Great skua eggs were collected in Shetland under licence. Collection took place in early June and one egg was taken at random from 30 nests. The length and breadth of the eggs was measured to 0.1 mm accuracy using dial callipers and they were weighed to the nearest gram. Eggs were wrapped in aluminium foil and stored at −20 °C. Frozen egg contents were homogenised, weighed, and freeze dried to constant mass.

In order to express the contaminants in wet weight concentrations, the percentage moisture content of the eggs was calculated. The 1980 eggs were all freshly laid and contained no embryo development so the moisture content was calculated using mass loss from freeze drying. Some of the 2008 eggs contained small embryos, so the moisture content of these eggs at laying was estimated from egg measurements and density of fresh Great skua eggs (Furness and Furness, 1981).

2.2. POP analyses

POPs and lipids were extracted using a micro-extraction technique as detailed in Daley et al. (2009). One ml of sample extract was removed for the gravimetric determination of neutral lipids (Drouillard et al., 2004). Sample clean up on the remaining extract was performed by florisil chromatography as described by Lazar et al. (1992). Extracts were concentrated to 1 ml by rotary evaporator and added to gas chromatography vials. Samples were analyzed for individual organochlorines by gas chromatography electron capture detection (GC-ECD) (Lazar et al., 1992). For each batch of six samples, a reference homogenate, method blank, external PCB standard (Quebec Ministry of Environment Congener Mix; AccuStandard, New Haven, CT, USA), OC standards and PCB 30 recovery standard were analyzed. Recoveries of PCB #30 in samples averaged (±SD) 82.5 ± 9.4%. Recoveries of individual PCB congeners in the inhouse reference tissue extracted with each batch of samples were within two standard deviations of the mean laboratory database value derived from laboratory control charts from the Great Lakes Institute for Environmental Research (GLIER) accredited organic analytical laboratory (Canadian Association for Environmental Analytical Laboratories Accreditation and ISO17025 certified) established by standard cold column extraction techniques.

A Hewlett–Packard HP 6890 gas chromatograph coupled with a Waters GCT-premier Time of Flight (TOF) mass spectrometer was used for PBDE detection and analysis. The gas chromatograph was equipped with a DB5 column; 30 m × 0.25 mm. I.D. × 0.25 μm – film thickness (J&W Scientific) and 7673 autosampler. Helium was used as the carrier gas: (UHP) with a flow rate of 1 ml/min and column head pressure of 69 psi. The sample (1 μl) was injected under splitless injection mode using an injection inlet temperature at 250 °C. The oven program began at 90 °C held for 1 min, followed by a ramp of 20 °C/min to 150 °C, followed by a second ramp of 4.5 °C/min until a temperature of 280 °C and held at the final temperature for 10 min. The GC–TOF was operated in EI mode at 70 eV following daily tuning and mass resolution calibration using Metri (68.9952, 121.0014, 189.9966, 265.9965, 284.9949) calibration solution. The 284.9949 ion was used as the lock mass during sample runs.

For each batch of samples extracted, the sample injection sequences were set in the following manner: 5 external standard calibration curve for PBDEs (Wellington Laboratories certified PBDE native mixture), internal recovery standard, sample blank, internal reference homogenate (GLIER Detroit River Fish pool) and 6 samples. Post processing of HR-MSD output was performed using QuanLynx software. The three dominant ions for analytes (BDE-17, 28, 49, 47, 66, 100, 99, 85, 154, 153, 138 and 183) were extracted from the total ion chromatogram over a window of ±10 s from the expected analyte retention time. Peak areas were quantified using the analyte response relative to the external standard calibration curve.

Toxaphenes (parlar 26, 50, 62 (Accustd, USA)) were analysed by GC-ECD in the University of Iceland using the extracts from GLIER, as in Olafsdottir et al. (2005).

2.3. Stable isotope analysis

Lipid-extracted pulverized samples were weighed into 0.5 mg tin capsules and analyzed with a Delta V Advantage isotope ratio mass spectrometer (Thermo Electron Corporation, Bremen, Germany) and 4010 Elemental Combustion System (Costech Instruments, Valencia, CA, USA). Stable isotope abundances are expressed in delta (δ) values as the deviation from standards in parts per thousand (‰) from the following equation:

$$\delta^{15}\mathrm{N} \text{ or } \delta^{13}\mathrm{C} = \left(\frac{R_{\mathrm{sample}}}{R_{\mathrm{standard}}}\right)^{-1} \times 1000 \quad (1)$$

where R is the ratio $^{15}N/^{14}N$ or $^{13}C/^{12}C$. The standard reference material was Pee Dee Belemnite carbonate for CO_2 and atmospheric nitrogen N_2. The analytical precision based on the standard deviation of two standards (NIST 8414 bovine muscle and internal lab fish muscle) for $\delta^{15}N$ ranged were 0.132–0.16‰, respectively, and for $\delta^{13}C$ ranged from 0.12‰ to 0.09‰, respectively, during the analysis of these samples. The analysis of NIST standards (sucrose and ammonia sulphate; $n = 3$ for each) during the analysis of samples generated values that were within 0.01‰ and 0.07‰ of certified values for $\delta^{15}N$ and $\delta^{13}C$, respectively.

2.4. Contextual data

Breeding success of Great skuas was estimated using standard methods (Walsh et al., 1995) in Foula, Shetland to compare data from the 1970s and 1980s (Hamer

and Furness, 1991; Phillips et al., 1997) with data from 2006 to 2008. Diet was monitored by collecting regurgitated pellets of indigestible prey remains from breeding territories and club sites on Foula during June and July (which includes most of incubation and chick-rearing). Egg volume indices were calculated as egg length times breadth^2 in order to compare egg size between years, since smaller eggs may reflect a scarcity of food for breeding birds. Pellets were classified to major prey type based on visual inspection, comparison with a reference collection of remains, and guide books to identify fish taxa from bones and otoliths. Data on pellet composition of great skuas in Shetland have been reported in a number of papers (Ratcliffe et al., 1998; Votier et al., 2004, 2008). Here we present data relating to the two time periods when eggs were sampled for pollutant analysis.

2.5. Statistical analyses

Univariate statistical analysis was carried out using Minitab (version 15). Percent lipid did not correlate with POP levels so data were analysed on a wet weight basis. POP data were log transformed and then tested for normality (Kolmogorov–Smirnov test). Where data failed that test we analysed using non-parametric tests. To allow comparisons with previously published studies which often give only means, or only medians, we have presented both mean and median values in tables. Similarly, some studies present concentrations only in lipid terms or only in dry mass terms. We present moisture and lipid contents to allow conversion for comparisons. We repeated all statistical tests in dry weight and lipid weight terms although we only quote wet weight analyses here as conclusions were the same. To reduce the number of statistical tests carried out, PCB congeners were grouped according to persistence in homeotherms (Borgå et al., 2005). Since we predict that OCs would be higher in 1980 eggs and PBDEs would be higher in 2008 eggs, statistical tests of the null hypothesis were carried out as one-tailed tests. Where appropriate we applied Bonferroni corrections to p-values to account for repeated tests on the same dataset.

To evaluate differences between years and the influence of environmental variables on POP concentrations and patterns, the data were subjected to direct multivariate ordination analysis (redundancy analysis, RDA). RDA is similar to the indirect ordination method principal component analysis (PCA), but included explanatory variables as well as response variables. The RDA extracts axes (RA) minimizing the total residual sum of squares among all response variables (here POPs), and assigns scores to the samples that are linear combinations of the POPs and significant explanatory variables (Steffen et al., 2006). Significant variables were chosen by forward manual selection, using Monte Carlo permutation test with 499 unrestricted permutations and a significance level of $p < 0.05$. Year was entered as nominal explanatory variable (dummy variable, Lepš and Šmilauer, 2003), whereas δ^{13}C, δ^{15}N and % lipids were all entered as continuous explanatory variables. In the RDA of absolute concentrations, POPs concentrations were logarithmically transformed to reduce variance heterogeneity and skewness. To investigate POP pattern (similar to relative contribution of an individual OC to $\sum$OC) the data were standardised by norm. All POPs which were detected in less than 30% of samples in both years were excluded from multivariate analysis.

The differences in concentration and pattern were further explored through principal component analysis (PCA). For more detailed description of RDA, PCA and diagram interpretation see Lepš and Šmilauer (2003). Multivariate statistics were carried out using CANOCO 4.5 for Windows (Ter Braak and Šmilauer, 2002).

3. Results

Lipid content of eggs was 7.0% (s.d. 1.2, $n = 27$) in 1980 and 6.5% (s.d. 1.1, $n = 29$) in 2008. These means did not differ significantly (t-test $t = 1.74$, n.s.). Nor were there any significant correlations between % lipid and POP level in the same egg, either in the 1980 or in the 2008 samples. Moisture content of eggs was 78% (s.d. 1.4, $n = 27$) in 1980, and 80% (s.d. 1.3, $n = 29$) in 2008. Although the difference is small, the medians differed significantly (Mann–Whitney test, $W = 499.5$ $p < 0.001$).

Legacy POPs were mostly at significantly lower concentrations in 2008 than in 1980, and for those compounds not showing a significant decrease, the trend was consistently for lower concentrations in 2008 except perhaps for trans-nonachlor (Table 1). In contrast, PBDEs were generally at higher concentrations in 2008 than in 1980, with increases in PBDE-99, 100, 153 and 154 statistically

Table 1
Concentrations of Organochlorines in Great skua eggs from Shetland in 1980 and 2008 (μg/kg wet weight).

	1980 ($N = 27$)		2008 ($N = 29$)		Test statistic	P-value
	Median (min–max)	Mean[a] (SD)	Median (min–max)	Mean[a] (SD)		
QCB	0.9 (ND–2.5)	1.0 (0.5)	0.7 (0.2–1.6)	0.7 (0.3)	$T = 2.36$	0.011[b]
HCB	32 (6.7–77)	33 (17)	20 (ND–88)	23 (18)	$T = 2.45$	0.009[b]
OCS	3.3 (0.7–19)	4.4 (3.3)	1.1 (0.3–4.8)	1.4 (1.1)	$T = 5.48$	<0.001[b]
p,p′DDE	1799 (470–11575)	2769 (2716)	598 (254–4588)	924 (908)	$T = 5.33$	<0.001[b]
p,p′DDD	62 (14–223)	71 (49)	12 (2.5–41)	14 (10)	$T = 8.90$	<0.001[b]
p,p′DDT	109 (28–1448)	182 (269)	15.8 (2.5–63)	18 (15)	$T = 8.92$	<0.001[b]
Mirex	26 (6.7–93)	30 (18)	20 (3.3–110)	24 (20)	$T = 1.79$	0.039[b]
β-HCH	3.9 (1.0–22)	6.6 (5.6)	1.4 (ND–8.6)	1.8 (1.5)	$W = 1089.0$	<0.001[b]
γ-HCH	ND–0.1[c]	/	ND–0.1	/		
Trans-chlordane	ND–2.2	0.3 (0.6)	ND–1.0	0.2 (0.3)		
Cis-chlordane	8.8 (3.6–21.6)	9.9 (5.0)	5.9 (1.0–13.1)	6.1 (3.1)	$T = 3.45$	0.001[b]
Trans-nonachlor	86 (30–170)	91 (41)	77 (6.5–358)	103 (83)	$T = 0.38$	0.354[b]
Cis-nonachlor	31 (12–63)	31 (138)	20 (7.6–53)	22 (11)	$T = 2.87$	0.003[b]
Oxy-chlordane	26 (9.1–149)	34 (28)	15 (ND–207)	28 (42)	$T = 2.46$	0.009[b]
HC epox	12.8 (2.1–35.2)	14 (9.1)	6.9 (3.2–18.1)	8.0 (3.9)	$T = 2.76$	0.004[b]
Dieldrin	68 (24–146)	69 (32)	25 (12–54)	29 (12)	$T = 7.28$	<0.001[b]
PCB group I[d]	2364 (404–8860)	2954 (1930)	1060 (336–4391)	1452 (1095)	$T = 3.77$	<0.001[b]
PCB group II[e]	1096 (180–5390)	1517 (1170)	384 (142–2194)	599 (507)	$T = 4.41$	<0.001[b]
PCB group III[f]	346 (68–1735)	486 (376)	113 (33–549)	161 (130)	$T = 5.48$	<0.001[b]
PCB group IV[g]	148 (37–665)	185 (135)	42 (23–164)	53 (35)	$W = 1084$	<0.001[b]
PCB group V[h]	81 (ND–477)	111 (102)	39 (ND–149)	44 (43)	$W = 966$	<0.001[b]
ΣPCBs	4175 (751–17855)	5544 (3816)	1614 (620–7492)	2405 (1829)		
Toxaphene 26[i]	82 (24–282)	95 (74)	26 (17–56)	32 (15)	$T = 3.79$	<0.001[b]
Toxaphene 50[i]	157 (69–619)	206 (162)	67 (39–125)	72 (31)	$T = 3.77$	<0.001[b]
Toxaphene 62[i]	52 (14–132)	52 (35)	16 (5.4–47)	20 (13)	$T = 3.06$	<0.001[b]

[a] Arithmetic mean.
[b] Bonferroni corrected critical P-value 0.0023.
[c] OCs with all values in a year below MDL (PCBs 0.01–0.08 μg/kg, Toxaphenes 0.5–1.0 μg/kg and all other OCs 0.01–0.05 μg/kg) are reported as ND and those with median below MDL are reported ND-maximum value. HCH measured but was below MDL in all samples.
[d] PCB Group I – congeners 153, 187, 183, 180, 191, 201, 194, 205, 206, 209.
[e] PCB Group II – congeners 99, 138, 128, 177, 170.
[f] PCB Group III – congeners 74, 118, 158.
[g] PCB Group IV – congeners 18/17, 33, 52, 49, 44, 70, 101, 110.
[h] PCB Group V – congener 149.
[i] $N = 10$ for both years.

Table 2
Concentrations of PBDEs in Great skua eggs from Shetland in 1980 and 2008 (μg/kg wet weight).

	1980 ($N = 26$)		2008 ($N = 27$)		Test statistic	*P*-value
	Median (min–max)	Mean[a] (SD)	Median (min–max)	Mean[a] (SD)		
PBDE-3	ND–7.82[c]	ND	ND	ND		
PBDE-15	ND–0.536	ND	ND	ND		
PBDE-28	ND–6.97	0.736 (1.42)	ND–6.59	1.20 (1.53)		
PBDE-47	83 (3.99–1314)	227 (351)	127 (34–541)	171 (145)	$T = -1.69$	0.050[b]
PBDE-49	ND–150	20 (37)	11.6 (ND–52)	16.7 (12.3)	$W = 586.0$	0.020[b]
PBDE-66	ND	ND	ND–4.13	ND		
PBDE-77	1.10 (ND–26)	3.10 (5.70)	2.04 (ND–6.51)	2.45 (1.63)	$W = 604.5$	0.041[b]
PBDE-99	2.04 (ND–22)	4.31 (5.47)	7.62 (3.57–43)	11.1 (8.66)	$W = 463.0$	<0.001[b]
PBDE-100	3.52 (ND–33)	6.61 (8.34)	10.7 (1.69–70)	16.1 (17.2)	$T = -3.89$	<0.001[b]
PBDE-119	ND	ND	ND–9.32	0.748 (2.23)		
PBDE-138	ND–0.686	ND	ND	ND		
PBDE-153	ND–4.99	0.605 (1.11)	6.63 (2.43–32)	9.24 (7.56)	$W = 363.0$	<0.001[b]
PBDE-154	ND–2.95	0.520 (0.745)	7.92 (3.68–33)	10.6 (7.43)	$W = 351.0$	<0.001[b]
PBDE-183	ND	ND	ND–0.838	ND		
∑PBDE	99 (5.07–1549)	264 (407)	173 (55–734)	240 (194)		

MDL values for PBDEs: 3 (0.328 μg/kg), 7 (0.476 μg/kg), 15 (0.322 μg/kg), 17 (0.561 μg/kg), 28 (0.567 μg/kg), 47 (0.373 μg/kg), 49 (0.782 μg/kg), 66 (0.476 μg/kg), 71 (0.356 μg/kg), 77 (0.666 μg/kg), 85 (0.545 μg/kg), 99 (0.471 μg/kg), 100 (0.361 μg/kg), 119 (0.430 μg/kg), 126 (0.709 μg/kg), 138 (0.612 μg/kg), 153 (0.488 μg/kg), 154 (0.420 μg/kg), 156 (0.753 μg/kg), 183 (0.638 μg/kg), 184 (0.564 μg/kg), 191 (0.709 μg/kg), 196 (1.498 μg/kg), 197 (1.396 μg/kg).

[a] Arithmetic mean.

[b] Bonferroni corrected critical *P*-value 0.007.

[c] PBDE congeners with all values in a year below MDL are reported as ND and those with median below MDL are reported as ND-maximum value. PBDE 7, 17, 71, 85, 126, 156, 184, 191 and 196 were below detection limits in all samples.

significant (Table 2) but not PBDE-47, which was the most abundant congener both years. PBDE-49 appears to have decreased but there is a very high standard deviation, especially in 1980. RDAs of POP concentrations and pattern resulted in year or $\delta^{13}C$ as significant (all p-values < 0.002) explanatory variables due to co-linearity (Monte Carlo, concentration $F = 22.0$ and $F = 20.0$ and pattern $F = 7.4$ and $F = 5.83$ for year and $\delta^{13}C$ respectively). Principal component analysis of concentration shows clear separation of the samples from the two years (Fig. 1) mostly along PC1, with legacy POPs, particularly DDT and the least persistent PCB congener (P5) in 1980 driving this trend, and PBDEs higher in 2008. The PCA of the POP pattern in the eggs shows that there is less separation between the years than for concentration (Fig. 2). The main drivers of sample separation are the proportionally higher DDE contribution to the 1980 eggs and the higher proportion of the most persistent PCBs (P1) in the 2008 eggs. Toxaphenes correlate with other legacy pesticides in concentration and pattern analysis but are not presented in Figs. 1 and 2 due to the smaller number of samples analysed.

Pellet analysis shows that undersized Haddock *Melanogrammus aeglefinus* and Whiting *Merlangius merlangus*, which being demersal fish and so not naturally available to surface-feeding seabirds are presumed to be scavenged discards from fishing vessels around Shetland, formed the majority of the pellets sampled in both periods (Table 3). However, Sandeels have become less frequent in pellets, while Herring and Mackerel, birds, and "other" prey have increased. There was little or no difference in $\delta^{15}N$ between samples, but a significant shift in $\delta^{13}C$ (Fig. 3). The differences between these egg samples were small compared to variation seen between different individual prey types and even between Sandeels of different sizes or geographic locations (Fig. 3). We can expect organochlorine levels to increase with $\delta^{15}N$ since this isotopic signal increases with trophic level (Käkelä et al., 2007). Birds feeding at higher trophic levels should accumulate more organochlorines since these biomagnify up the food web (Fisk et al., 2001). All 43 organochlorines where data were normally distributed showed positive Pearson correlations between organochlorine concentration and $\delta^{15}N$ in individual eggs from the 1980 sample (1-tailed binomial test $p < 0.001$); ten of these were individually significant relationships at $p < 0.05$. For the 2008 sample, 27 out of 42 correlations were positive and 15 were negative, suggesting a weaker relationship with $\delta^{15}N$. Indeed, no individual correlation was statistically significant, but the expectation from a null hypothesis of no relationship between $\delta^{15}N$ and organochlorine level would be that half of the correlations would be positive and half negative. The data deviate significantly from that prediction with an excess of positive correlations (1-tailed binomial test $p = 0.044$), indicating that birds feeding at higher trophic level do indeed have higher concentrations of organochlorines in their eggs. Carbon isotopes show a contrasting pattern between samples. In the 1980 eggs, $\delta^{13}C$ showed a positive correlation with organochlorine concentration for 41 out of 43 cases (2-tailed binomial test

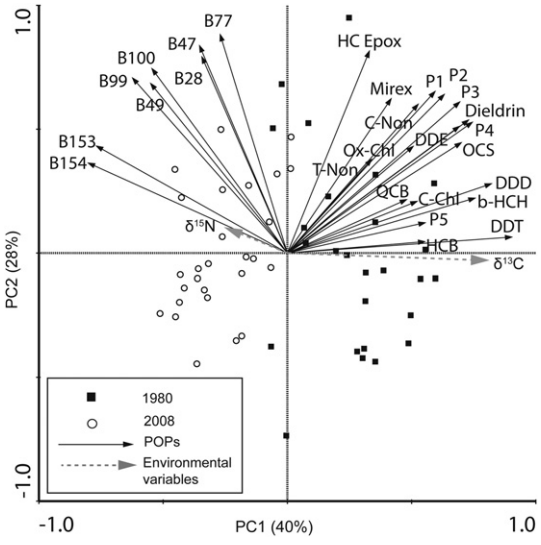

Fig. 1. Indirect multivariate ordination analysis diagram of POP concentrations in Great skua eggs from Shetland 1980 and 2008. Percentage of variation explained by each principal component (PC) is given in brackets on each axis. The length of each arrow indicates the amount of variation in that POP amongst the samples, longest arrows showing greatest variation. The angle between each arrow and between arrow and axis indicates the degree of correlation, the closer the arrows the more highly correlated they are. Abbreviations: T-Non (Trans-Nonachlor), C-Non (Cis-Nonachlor), Ox-Chl (Oxy-Chlordane), P1–P5 (PCB groups 1–5).

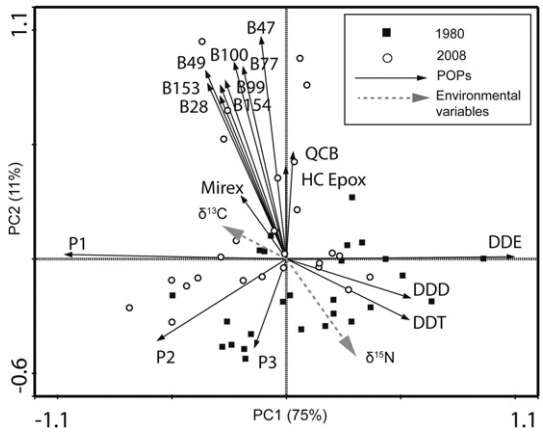

Fig. 2. Indirect multivariate ordination analysis diagram of POP pattern in Great skua eggs from Shetland 1980 and 2008. Percentage of variation explained by each principal component (PC) is given in brackets on each axis and inclusion rules were set to 10%. Abbreviations: P1–P3 (PCB groups 1–3), B indicates PBDE congener.

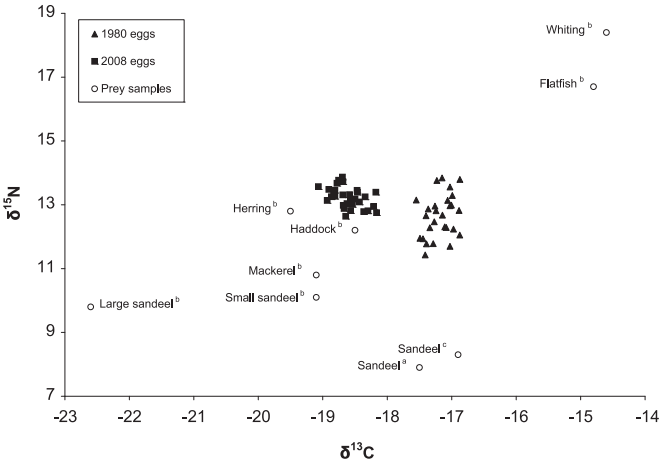

Fig. 3. Stable carbon and nitrogen stable isotope measurements of 1980 and 2008 Great skua eggs from Shetland together with published data on stable isotope signatures of prey: Käkelä et al., 2007[a]; Bearhop et al., 1999[b], 2002[c]; Thompson and Furness, 1995[d].

$p < 0.001$). In the 2008 eggs, $\delta^{13}C$ showed a negative correlation with organochlorine concentration for 41 out of 42 cases (two-tailed binomial test $p < 0.001$).

The sizes of Great skua eggs have changed significantly over the study period, with eggs in 2008 at a volume index of 157, the smallest recorded in any year in Shetland and about 10% smaller than eggs laid in the 1970s or 1980s (Furness, 1987; Hamer and Furness, 1991). Similarly, breeding success of Great skuas was consistently high in the 1970s and early 1980s (averaging 1.1 chicks per pair), but low to moderate in 2006–2008 (0.3–0.8 chicks per pair). Low breeding success and smaller egg size in 2006–2008 correlate with a scarcity of Sandeel in pellets, and increased feeding on birds, Herring, Mackerel, and "other" prey (Table 3).

4. Discussion

In general, both of our main hypotheses were supported: Levels of legacy POPs decreased between 1980 and 2008; levels of PBDEs increased. The apparent decrease of PBDE-49 may be a sampling error given the high standard deviations, or might possibly reflect the early phasing out of tetra and penta PBDEs in Europe and North America. We found no significant correlations between lipid concentration in individual eggs and the POP levels in the same egg in either of the years sampled. Lipid levels in our samples were similar to those reported by Bloch et al. (unpubl. MS) who found a lipid content of 7.5% (s.d. 1.2) for 19 Great skua eggs collected in the Faroes in 1977. Great skua eggs have rather low lipid content compared to eggs of other seabird species (Braune, 2007; Helgason et al., 2008; Lavoie et al., 2010). Standardising POP concentrations to lipid mass would increase the apparent contamination of Great skuas given the low lipid level in their eggs. Lipid levels in eggs also decrease through the incubation period, so that comparisons between eggs that have been incubated for different numbers of days create differences in lipid-corrected contaminant concentrations that may complicate comparisons between studies (Peakall and Gilman, 1979).

Table 3
Types of pellets cast by Great skuas at Foula, Shetland during the two time periods when eggs were sampled for POP analyses.

Parameter	1978–1980	2006–2008
Number of pellets sampled	300	484
% Discards (mostly haddock and whiting)	54	70
% Sandeel	41	0
% Herring and mackerel	0	9
% Bird	3	13
% Other (mostly mammals, goose-barnacles)	2	8

Furness and Hutton (1979) reported organochlorine levels in 12 Great skua eggs collected in Shetland in 1976. Those contained means of 80 μg/kg wet weight of dieldrin (range 20–150), 1700 μg/kg wet weight DDE (range 400–3600) and 17,600 μg/kg wet weight ∑PCB (range 6100–36,000). Furness (1987) reported levels in 6 eggs from Shetland sampled in 1983 as 40 μg/kg wet weight of dieldrin, 530 μg/kg wet weight of DDE (range 400–1610) and 6100 μg/kg wet weight of ∑PCB (range 2800–17,000). Bloch et al. (unpubl. MS) reported means of 75 (s.d. 100) μg/kg dieldrin, 6100 (s.d. 2900) μg/kg DDE, and 35,900 (s.d. 18,100) μg/kg ∑PCB from the nearby Faroe Islands. However, these data from the 1970s and early 1980s, despite being measured on much less sophisticated analytical equipment of the time, agree very well with our data for 1980 eggs analysed in 2009, with the possible exception of ∑PCB which was somewhat higher in all the samples listed above than in our data (Table 1). That difference could be influenced by how the sum of PCBs was calculated in different studies.

There are no previous data for PBDEs in Great skua eggs. However concentrations of six PBDEs in Herring gull eggs from Northern Norway in 1983, 1993 and 2003 (457 s.d. 278; 759 s.d. 526; 570 s.d. 225 μg/kg lipid wt) were all lower than the same sum of PBDEs for 1980 and 2008 (3491 s.d. 5342; 3667 s.d. 3930 μg/kg lipid wt) Great skua eggs. This is mostly driven by higher levels of PBDE-47 in Great skuas, (Herring gull 350 s.d. 215; 497 s.d. 294; 412 s.d. 191; Great skua 3307 s.d. 5122; 2861 s.d. 3075). The few studies there are of temporal trends of PBDEs in seabird eggs suggest that levels of tetra- and penta-BDEs started to decline in the mid 1980s–1990s in Europe (Helgason et al., 2009; Sellstrom et al., 2003).

It is unclear whether concentrations of POPs in these samples reach toxic levels, but this seems possible. With regard to reproductive success, Tillitt et al. (1992) reported a lowest observable effect concentration of 3500 μg/kg wet weight ∑PCB in double-crested cormorants *Phalacrocorax auritus*. More than half of the Great skua eggs sampled in 1980 exceeded that threshold, as did a few of the 2008 eggs. The highest ∑DDT levels in 1980 (12,000 μg/kg) and in 2008 (4600 μg/kg) equal or slightly exceeded thresholds that are associated with eggshell thinning and impair breeding success in waterbirds (2500–8000 μg/kg; Custer et al., 1999).

Can the change in POP concentrations from 1980 to 2008 be attributed to ecological differences rather than to a change in environmental contamination? A strength of our study is that we can

provide the context of ecological data on Great skuas in Shetland. The smaller egg size and low breeding success of Great skuas in recent years suggest that birds may now be in poorer body condition and stressed by food shortage while breeding. Such changes could result in more reliance on body fat to fuel egg production and that could mobilise more contaminants into eggs compared with birds that are in good condition and have unconstrained supplies of food. However, we found no significant difference in lipid concentrations between 1980 and 2008 eggs, and only a very small difference in water content. The latter may be a consequence of differences in sampling and egg storage procedures between years.

Changes in diet as indicated by pellets, and by $\delta^{13}C$ changes, could also influence POP levels in the eggs. Sandeels are short-lived fish that feed at a low trophic level and tend to accumulate only low concentrations of POPs (Shore et al., 2006). Discards taken by Great skuas at Shetland are predominantly 20–25 cm Haddock and Whiting and small flatfish. These demersal fish tend to accumulate higher concentrations of POPs than found in Sandeels (Food Standards Agency, 2006). While pellets indicate that Great skuas have fed extensively on discards throughout the period, the pelagic fish in their diet has changed. They have taken fewer Sandeels in recent years and have taken Herring and Mackerel which were not seen in the diet in the 1970s or 1980s (Votier et al., 2004). These changes in diet reflect changes in pelagic fish abundance in the region.

The switch of the correlation between $\delta^{13}C$ and organochlorine concentration from positive in 1980 to negative in 2008 suggests that the predominant source of organochlorines changed between these periods. In 1980, the positive correlation implies that most organochlorines were accumulated from feeding on discards (which have an enriched $\delta^{13}C$). The negative correlation in 2008 implies that birds accumulating most organochlorines were feeding more on Herring and Mackerel than on discards. This would suggest that adult Herring and Mackerel accumulate more organochlorines than found in undersized Haddock, Whiting and flatfish and this is indeed the case (Food Standards Agency, 2006).

Legacy POPs decreased in concentration in eggs from 1980 to 2008. This is the opposite to the trend predicted by a shift in diet from Sandeel to Herring and Mackerel, so strengthens confidence in the view that these changes are a result of historical bans and reduced use of these compounds, and thus lower levels in the environment. Comparing median levels in 2008 with those in 1980, decreases were very high for DDT (85%) and PCB group IV (72%), less for DDE (67%), dieldrin (63%), PCB group II (65%), PCB group III (67%), and only 55% for PCB group I. These differences fit with the persistence of these different compounds, the largest decreases being seen with the compounds that are least persistent.

A switch in diet from Sandeel to Herring and Mackerel could be partly responsible for the measured increases in PBDEs in Great skua eggs. We conclude that there is a need for further investigation of trends in PBDE levels in the marine ecosystems of the NW Atlantic.

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