Identifying the provenance of Leach's storm petrels in the North Atlantic using polychlorinated biphenyl signatures derived from comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry

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Abstract

PCB signatures can be used for source identification, exposure studies, age dating and bio-monitoring. This study uses comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GCxGC-ToFMS) to produce a PCB signature comprised of over 80 PCBs for individual Leach's storm petrels (*Oceanodroma leucorhoa*). The Leach's storm petrel is a relatively small, elusive, understudied pelagic bird, which only returns to remote islands under darkness during the breeding season. Samples were obtained from 25 Leach's storm petrels found dead in Canada and the UK following storm events in 2006 and 2009. Tissue samples were extracted and analysed by GCxGC-ToFMS and results showed that 83 PCB congeners were present in >60% of samples. An assessment of the PCB signature in four different tissue types showed that it did not vary greatly in samples obtained from the gut, heart, liver and stomach. Multivariate statistical analysis identified a distinctive PCB signature in birds from Canada and Europe which was used to identify the regional provenance and transatlantic movement of individual birds. The findings showcase the ability of GCxGC-ToFMS to provide the high quality congener specific analysis that is necessary for PCB fingerprinting, as well as highlighting the potential of PCB signatures for use in ecological studies of movement, foraging and behaviour.

Key Words

Polychlorinated biphenyl (PCBs); Leach's storm petrel; Comprehensive two-dimensional gas chromatography, Time of flight mass spectrometry; Chemical fingerprinting.

1. Introduction

1.1 PCB distribution and signatures in animals

Polychlorinated biphenyls (PCBs) are a group of 209 man-made compounds that were first synthesised in the late 1800s and commercially produced in 1929 (Johnson et al., 2006). They were used extensively throughout the 20th century for a variety of industrial uses. PCB production in the United States peaked in 1970 (Durfree et al., 1976). However, production decreased steadily throughout the 1970's due to a better understanding of the health and environmental risks associated with PCBs. Phasing out began in 1976 in the United Kingdom (UK) (Creaser et al., 2007) and in 1977 in Canada (Environment Canada, 2013). Today policy is largely conducted within an international framework, e.g. the Stockholm convention on persistent organic pollutants aims to eliminate PCB production and use and achieve environmentally sound management of PCBs by 2028 (UNEP, 2013). While PCBs have been largely phased out of commercial/industrial use, they are highly persistent in the environment and are still used in some countries in closed system applications, such as dielectric fluids in electrical equipment. Despite the reduction in PCB inventories and implementation of legislative controls on PCB use, releases to the environment still occur. Coupled with the high persistence of PCBs means they remain contaminants of concern which are found in organisms all over the globe. Investigations involving PCBs often focus on determining the concentrations of the most toxic PCBs (the 12 dioxin like congeners (WHO12)) and/or the most commonly detected PCBs (the European Union 7 indicator congeners (EC7)). Whilst this may be appropriate when determining a health risk or performing simple screening exercises, potentially useful data on the PCB signature is lost as only a fraction of the total number of PCBs present are quantified. Through appropriate sample preparation and analysis by comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GCxGC-ToFMS), over 130 PCBs have been detected within tissue samples (whiting liver) and used to create a detailed PCB signature (Megson et al., 2013a).

PCBs can enter the environment through intentional discharges, unintentional spillages and leaks and aerial deposition. Once they have been released into the environment they can undergo further cycling and long range transport. However, the global distribution of PCBs is far from homogenous and different regions of the globe have different total PCB concentrations and specific PCB signatures (Jaspers et al., 2013; Meijer et al., 2003). Variations in PCB signatures have been recorded in a wide variety of different animals (Hansen, 1999; Jaspers et al., 2013), which are believed to be primarily linked to the diet. Specific signatures have been recorded for different species of birds that consume various prey, e.g. fish, insects, mammals and other birds (Hansen, 1999; Jaspers et al., 2006). Variations in PCB signatures have also been used to identify different sub-populations of the same species feeding at different tropic levels. This has been demonstrated for Arctic mammals such as seals and walruses as well as seabirds (Hansen, 1999; Muir et al., 1995; Roscales et al., 2011).

Most PCBs are present in animals in relatively low concentrations. This has often restricted investigations to techniques involving destructive tissue sampling so that analysis can be undertaken on lipid rich tissue or eggs. Among ornithological research, novel techniques, such as the analysis of feathers, have been used for non-destructive biomonitoring but only the most abundant PCB congeners are commonly detected (Dauwe et al., 2005; Jaspers et al., 2007). Therefore, due to ethical reasons and analytical limitations, few studies have used birds to investigate regional and geographical patterns of PCB contamination. Most studies have focused on non-migratory passerine species such as starlings (Eens et al., 2013), as they are a non-migratory and, as such, are well suited for monitoring local contamination. Contamination profiles are expected to better reflect local contamination because of their relatively small home ranges, territories and foraging areas (Eens et al., 2013). Less research has been undertaken on the PCB signature of hard to study species such as seabirds that operate over very large spatial scales.

1.2 Leach's storm petrel

The Leach's storm petrel (*Oceanodroma leucorhoa*) is a small (wingspan 450 to 480 mm, weight 35 to 45 g) pelagic bird that breeds on remote islands (Huntingdon et al., 1996). Despite being globally abundant (>10 million breeding pairs), elusive habits such as nocturnal visits to colonies and pelagic foraging mean that aspects of its ecology remain unknown. In the North Atlantic there are breeding colonies in North America and Western Europe (Figure 1). Newfoundland, Canada supports the largest breeding colonies (Huntingdon et al., 1996; Robertson et al., 2006) and the European colonies are predominantly divided between two small island archipelagos in Iceland (Vestmanyjaer) and Scotland (St Kilda) (Mitchell et al., 2004).

Although they spend much of their time at sea, large numbers of Leach's storm petrel can be driven onshore during severe storm events. Many of these birds are discovered either dead or moribund, which presents an opportunity to undertake detailed assessments on carcasses and investigate their origin. During 2006 and 2009 a series of storm events in waters around the UK and Canada drove many Leach's storm petrels inland. Twenty five carcases were obtained from wrecked birds that had been killed by these storms and subsequently recovered by members of the public. Twelve were recovered from Newfoundland and 13 from the UK. It was unclear if the wrecked birds discovered in the UK and Newfoundland were from local colonies, or from a combination of different breeding colonies widely spread across the North Atlantic. Tissue and feather samples were obtained from these wrecked birds and assessments of provenance were undertaken using highly branched isoprenoid (HBI) concentrations and stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$). Analysis of HBI concentrations was able to distinguish between birds recovered from the UK and Newfoundland (see Table 1). HBIs provide recent dietary insights and the results indicate that the birds wrecked in the two areas were feeding locally in the weeks preceding the storms (Brown et al., 2013). Stable isotope ratios in a feather are linked to the prey consumed during the growth phase of that feather; therefore ratios are often used for

126 tracking the dispersal of migrant wildlife (Hobson, 2007). However, the results for feathers
127 obtained from the birds used in this study were inconclusive due to the mixture of feathers
128 available from the wrecked birds and similarity in the signatures from the two sub-
129 populations. (see Table 1) (Bicknell, 2011).

130 ### 1.3 Aim

131 Among marine predators, seabirds have been proposed as useful bio-indicators for PCBs
132 and other persistent organic pollutants, mainly because they are positioned at high trophic
133 positions, breed at specific locations and are widely distributed (Burger and Gochfeld, 2004).
134 However, much of this research on seabirds has focused on coastal species due to the
135 ethical and technical limitations of sampling strategies associated with pelagic species
136 (Elliott, 2005; Yamashita et al., 2007). This paper assesses PCBs in the highly pelagic
137 Leach's storm petrel using a recently reported GCxGC-ToFMS method for fingerprinting
138 PCBs in environmental samples (Megson et al., 2013a). This study aims to provide valuable
139 baseline data on PCBs in Leach's storm petrels from the North Atlantic and demonstrate the
140 potential of using PCB signatures as a tool for identifying the provenance of individual birds.

141 ## 2 Methodology

142 ### 2.1 Sample collection and preparation

143 The same set of carcasses that were analysed in previous studies undertaken by Bicknell
144 (2011) and Brown et al. (2013) were used in this study. This comprised 12 birds from
145 Newfoundland that were driven onshore during a storm event in early September 2006 (S-7
146 to S-18), 11 birds from the UK that were recovered after a storm in December 2006 (S-21 to
147 S-33) and two birds that were recovered from the UK after a storm in December 2009 (S-19
148 and S-20) (Figure 1). All carcases were discovered by members of the public and stored at -
149 80 ˚C prior to sampling in 2011. Individual organs could not be removed from the majority of
150 the samples due to partial decomposition. However, for one bird (S-22), decomposition was

not as severe and four specific organs were removed for analysis. Two organs were also removed from S-23 and S-24.

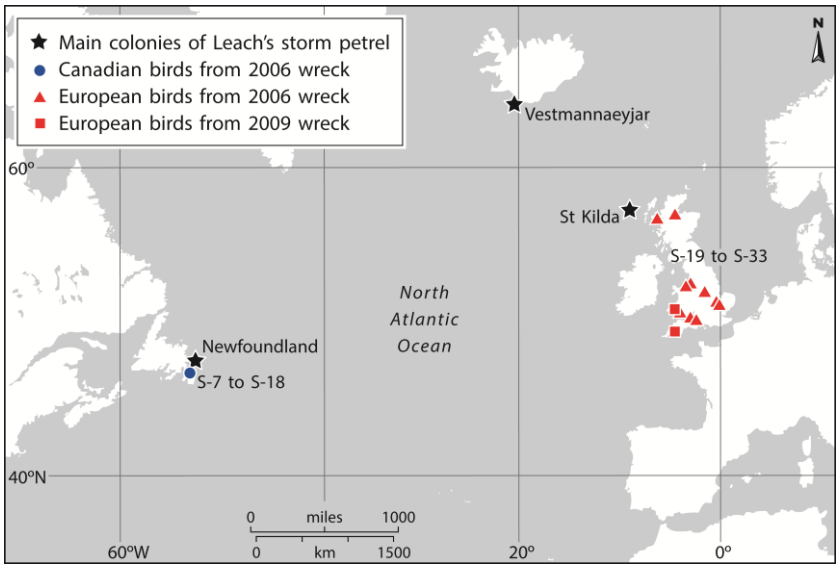


Figure 1. Location of the main Leach's storm petrel colonies and the sites from which wrecked birds were recovered during storms in 2006 and 2009. Twelve birds were recovered from Newfoundland (S-7 to S-18) and 13 birds from the UK in 2006 (S-21 to S-33) & 2009 (S-19 and S-20)

2.2 Extraction

Sample extraction was undertaken following the established method for PCB extraction in tissues reported by Megson et al. (2013a) and outlined in Brown et al. (2013). All samples were freeze-dried (-45 ˚C; 0.2 mbar; 72 h) and ground into a powder, internal standards were added and an organic extract obtained by adding dichloromethane/methanol (2:1 v/v) and ultrasonicating (8 x 10 min). Extracts were filtered, dried and re-suspended in hexane before being separated into a non-polar fraction by column chromatography (SiO_2). Samples were blown down to approximately 50 µL using nitrogen, left overnight in a clean environment to evaporate to dryness and reconstituted with 10 µL of $^{13}C_{12}$ internal standard (CIL-EC-5370 EN-1948-4 PCB sampling standard, LGC) and 90 µL of hexane prior to analysis by GCxGC-ToFMS.

2.3 GCxGC-ToFMS Analysis

2.3.1 Analytical procedure

Samples were analysed using the method described by Megson et al. (2013a) using a time-of-flight mass spectrometer, (LECO, St. Joseph, MI Pegasus 4D) coupled to a two dimensional gas chromatograph (Agilent Technologies 7890A) equipped with a thermal modulator (LECO, St. Joseph, MI). The gas chromatograph was installed with a Rtx-PCB (60 m x 0.18 mm x 0.18 µm) ^{1}D column and a Rxi-17 (1.5 m x 0.1 mm x 0.1 µm) ^{2}D column. A sample volume of 1 µL was injected in splitless mode. All data files were processed using ChromaTOF software set to identify 10,000 peaks with a signal-to-noise ratio of > 10:1. Throughout this paper PCBs are referred to using the Guitart numbering system (Guitart et al., 1993).

2.3.2 Data Quality

Analytical blanks were run with each batch of approximately 10 samples. All samples were spiked with a $^{13}C_{12}$ internal standard (CB-60, CB-127, CB-159) which was used to quantify PCB concentrations by isotope dilution. Concentrations were normalised to dry weight tissue mass and are therefore reported as ng g^{-1}. As samples were originally extracted for the analysis of HBIs, PCB recovery could not be accurately determined for each sample; therefore reported concentrations were not corrected based on sample recovery or lipid corrected. However, application of this method to other tissue samples (such as fat and blood) for the determination of PCBs consistently recorded recoveries in the range 30 – 60% (unpublished data), which meets the recovery requirements of US EPA method 1668C. Experiments using a 50:50 mixture of A1254:A1016 (at 500 µg L^{-1} total PCBs) showed no significant loss from the blow-down procedure for any of the PCBs analysed (recovery of 101 ± 3.4 %; 1 standard deviation). Limits of detection for individual PCBs were in the range 0.1 - 5 ng g^{-1} (dry weight). Accuracy and precision were measured for the sum of the European Union 7 indicator congeners (EC7) (CB-28, CB-52, CB-101, CB-118, CB-138, CB-153, CB-

180) by analysing a 10 mg L^{-1} Aroclor 1248 standard three times. The accuracy of the sum of the EC7 congeners for the three samples was 105 ± 0.9 % (1 standard deviation).

2.4 Statistical analysis

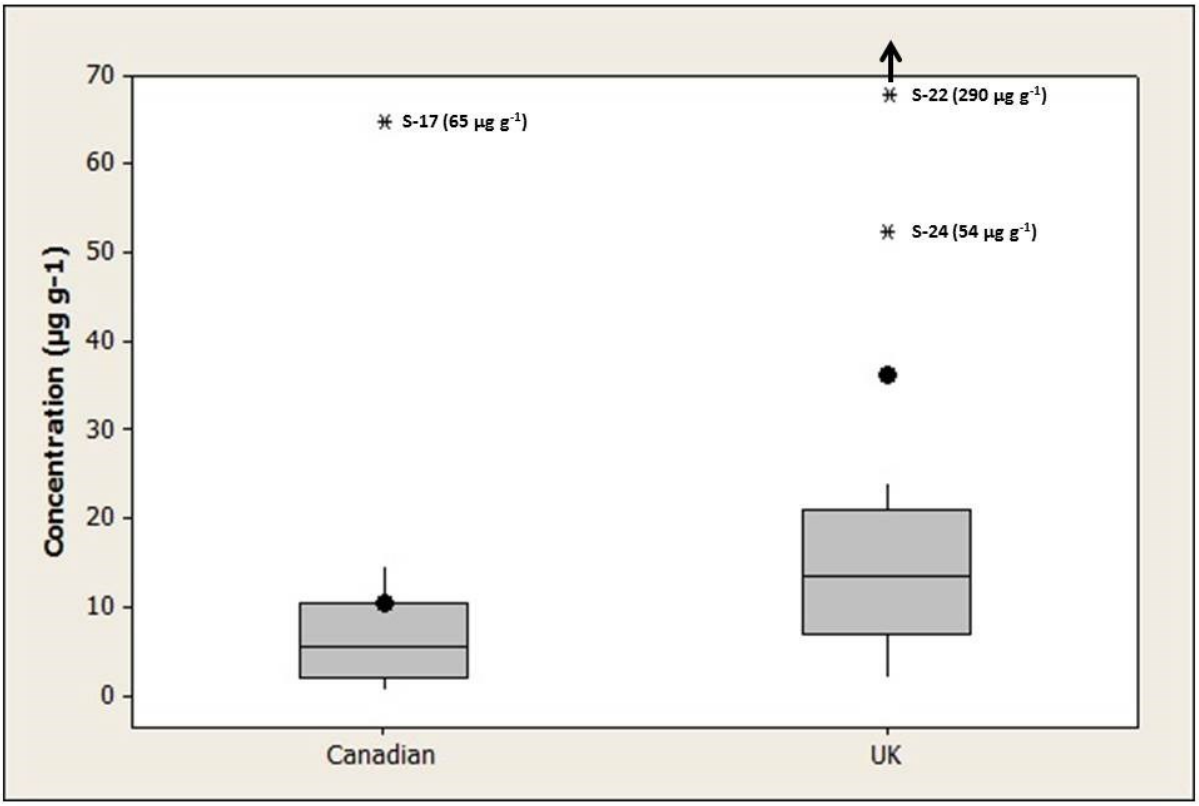
The results for the 25 storm petrels were subjected to principal component analysis (PCA). For the birds where individual organs were removed the results from each organ were included in the analysis. The samples denoted with; 'a' were obtained from the liver, 'b' from the stomach, 'c' from the guts and 'd' from the heart. Where a PCB was not detected it was included in the dataset as a '0'. As part of the data quality check, other values were substituted for '0', but these had no observable effect on the data output and so the '0's were retained. To reduce any bias from a high proportion of non-detects for a specific congener, PCBs that were not detected in over 60% of samples (i.e. PCBs present in less than 18 out of the 30 samples) were removed from the analysis following the guidance of Helsel (2006). The resultant data set contained 30 samples and 83 PCBs. Before performing PCA the data were normalised by transformation to a percent metric to remove concentration/dilution effects. The data were then mean centred and scaled using a Z-transform (autoscale transform) to prevent high concentration variables from dominating the analysis (Johnson et al., 2007). The first three principal components explained 65.5% of the variance in the data set. Scatter plots showing goodness of fit on a congener-by-congener basis are shown in Supplementary Information (S1). These justify the use of a three principal component model over a two principal component model as they show the improvement in the goodness of fit for the more chlorinated congeners.

3 Results

3.1 PCBs in the Leach's storm petrel

The most dominant PCBs encountered in the samples were CB-153, CB-118, CB-138 and CB-180. In each sample these accounted for approximately 30%, 10%, 10% and 10% of the total PCB load respectively. PCB concentrations were calculated for the European Union 7

221 indicator (EC7) congeners and varied from 0.6 µg g^{-1} (S-12) to 290 µg g^{-1} (S-22). Total
222 concentrations of the EC7 congeners appeared to be greater in the birds found in the UK
223 (mean value of 36 µg g^{-1}) compared with the birds found in Canada (mean value of 11 µg g^{-1}),
224 although these differences were not statistically significant (Figure 2).



225

226 Figure 2. Box and whisker plots of the sum of European Union 7 indicator (EC7) congeners
227 in Leach's storm petrels found in Canada and the UK. The box shows the interquartile range
228 (25^{th} percentile to 75^{th} percentile), with the median as a horizontal line across each box and
229 the mean displayed as a black dot. Whiskers (lines) represent 1.5 times the interquartile
230 range and samples beyond the interquartile range are plotted as individual points.

231 The PCB concentrations are reported along with the results of the previous investigations
232 undertaken by Bicknell (2011) and Brown et al. (2013), in Table 1. While no correlation
233 between the PCB concentrations and stable isotope data was observed, there was a strong
234 positive correlation between the PCB and HBI concentration data (R^2 value of 0.7 and P

235 value of 0.006). Where possible the sex of the bird was also determined, however this was
236 not well correlated with the stable isotope, HBI or PCB data. PCB concentrations in birds
237 wrecked from the 2009 storm were slightly lower than the birds from the 2006 storm;
238 however there was no observable difference in the PCB signatures (see Section 3.3).

239 Table 1. Concentrations of ∑EC7 PCBs, HBIs (Brown et al., 2013) and stable isotope ratios
240 from Leach's storm petrels from the identified subgroups (Bicknell, 2011), concentrations
241 from separate organs of the same bird were averaged.

Sample	**∑EC7 PCBs ($\mu g\ g^{-1}$)**	**Total HBIs ($ng\ g^{-1}$)**	**$\delta^{15}N$ (‰)**	**$\delta^{13}C$ (‰)**	**Sex (M/F)**
Recovered from Canada					
S-7	3.1	-	15.3[a]	-20.0[a]	F
S-8	2.7	-	13.2[a]	-17.7[a]	F
S-9	6.0	0.22	15.2	-18.8	F
S-10	6.4	0.45	14.6	-19.0	F
S-11	1.8	0.21	14.2	-18.8	F
S-12	0.6	0.17	14.9	-19.2	F
S-13	5.0	-	14.9[a]	-19.9[a]	F
S-14	15	-	14.6[a]	-17.9[a]	F
S-15	1.0	-	-	-	F
S-16	9.7	-	14.7[a]	-18.9[a]	F
S-17	65	-	14.3[a]	-19.1[a]	F
S-18	11	0.42	13.7	-19.1	M
Average (1 σ)	10.6 (+/- 17.6)	0.29 (+/- 0.13)	14.5 (+/- 0.58)	-19.0 (+/- 0.19)	
Recovered from the UK					
S-22	290	4.7	15.0	-19.2	-
S-23	16	2.2	15.4	-19.1	-
S-24	52	4.2	14.7	-20.7	F

S-25	24	2.4	14.7	-19.1	M
S-26	15	1.2	14.2	-18.9	F
S-29	18	2.9	12.2	-19.1	F
S-19	4.3	-	13.4	-17.6	-
S-20	2.1	-	14.7	-18.3	-
S-21	6.6	2.7	14.2	-18.6	M
S-27	14	4.3	13.8	-19.8	-
S-30	7.4	0.9	14.6	-18.9	M
S-32	8.1	-	14.4	-19.1	F
S-33	13	2.6	12.7	-19.0	M
Average (1 σ)	36.2 (+/- 77.3)	2.8 (+/- 1.3)	14.2 (+/-0.92)	-19.0 (+/- 0.72)	

242 - = not analysed

243 [a] = Sample collection was targeted towards newly grown feathers (produced whilst the birds
244 were at their respective breeding grounds); however these birds had not finished moulting
245 and therefore the sample had to be obtained from an old tail feather rather than new one.

246 **3.2 PCB signatures in different organs**

247 Individual organs could not be removed from the majority of the samples due to partial
248 decomposition. However, where different organs could be removed the PCB signature
249 appeared to be similar in each organ, although the stomach contained higher proportions of
250 CB-190 and depleted proportions of CB-153 (Figure 3). The covariance in the signature of
251 the different organs can also be observed in the PCA scores plot (see Figure 4).

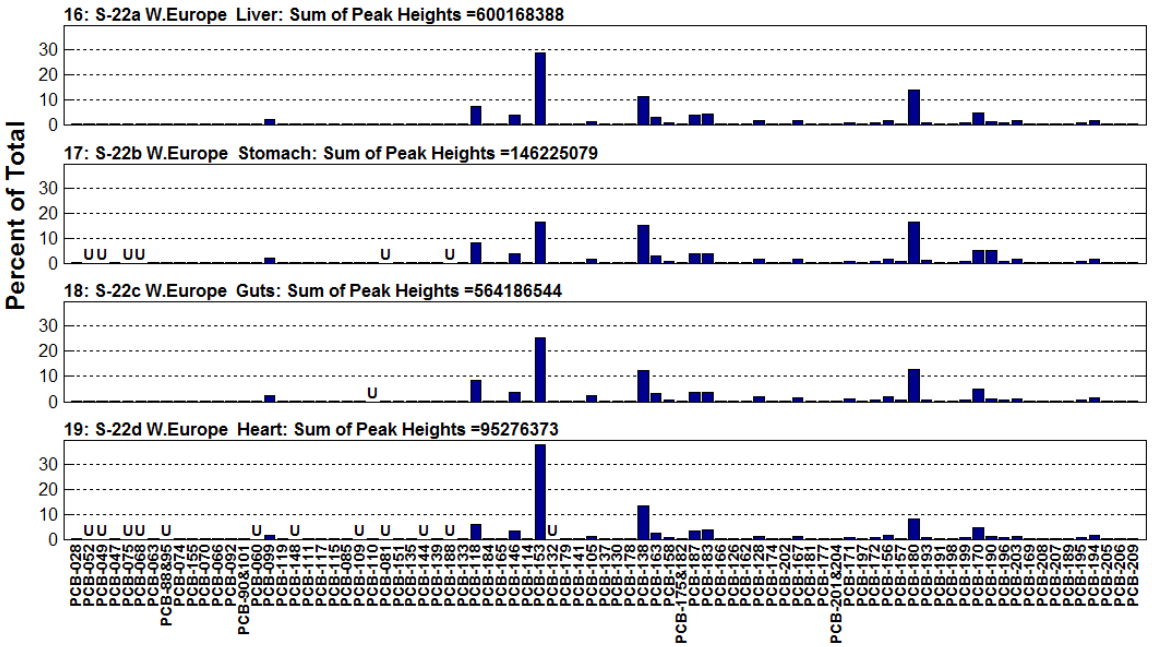


Figure 3. Congener plots showing differences in signature in liver, stomach, guts and heart from the same Leach's storm petrel found wrecked in the UK. 'U' represents a PCB present at a concentration below the limit of detection.

3.3 Identifying Leach's storm petrels wrecked in Western Europe and Canada

Three main groups of birds were identified through principal component analysis (Figure 4), with a gradation/mixing between the groups. The three groups were labelled as; Canadian group, Western European group 1 and Western European group 2. The Canadian group were separated by a positive score on principal component 2, whereas birds recovered from the UK predominantly had a negative score on principal component 2. The birds found in the UK were further subdivided as Western European group 1, based on a positive score on principal component 1 and Western European group 2 based on a negative score on principal component 1. A similar 3 end member system was also produced when the data were assessed using the unmixing model, polytopic vector analysis. This is a self-training, receptor modelling technique that can be used to resolve the following in a multivariate mixed chemical system; the most likely number of end members, the composition of each end member and the relative proportions of each end member in a sample (Johnson et al.,

2007). A ternary diagram of the mixing model results from the polytopic vector analysis is presented in Supplementary Information (S2).

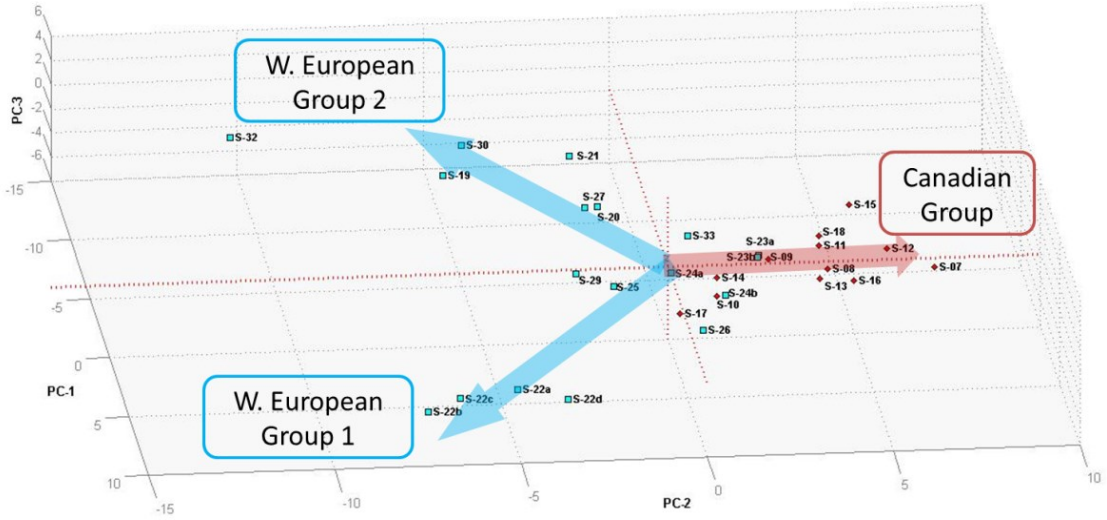


Figure 4. PCA scores plot showing three main groups of birds. Red dots represent birds found in Canada and blue dots represent birds found in the UK.

Although overlap between the different groups is apparent, the results reveal differences in the PCB signature in the birds recovered from Canada and the UK. The birds recovered from the UK had higher proportions of CB-138, CB-163, CB-187 and CB-184, whereas the birds recovered from Canada tended to have higher proportions of CB-153. The results also split the birds recovered from the UK into two sub-groups. Western European group 1 generally contained higher proportions of the more chlorinated congeners; CB-170, CB-180, CB-183 and CB-194 whereas the Western European group 2 birds generally contained higher proportions of the less chlorinated congeners; CB-66, CB-74, CB-99 and CB-105 (Figure 5).

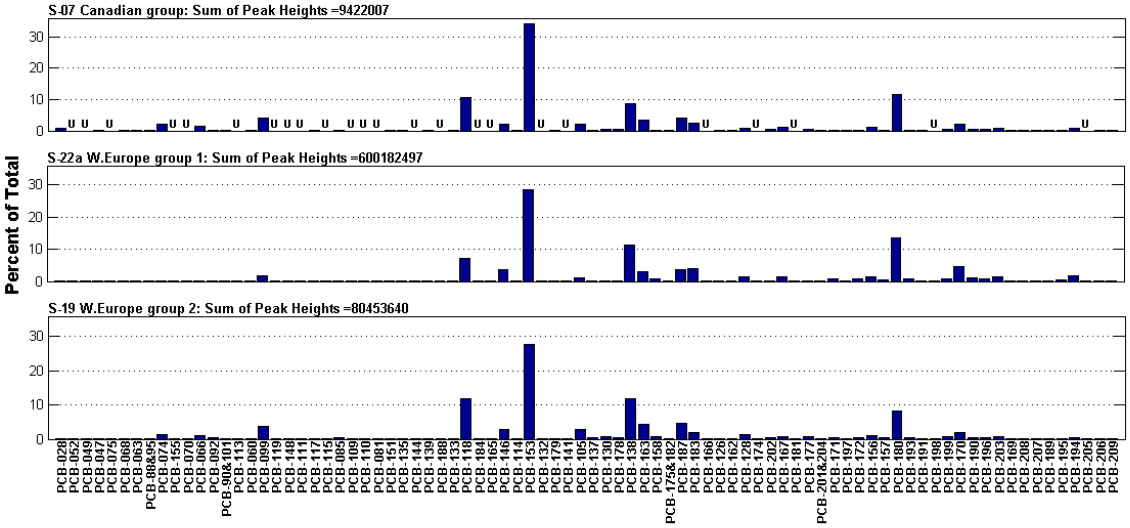


Figure 5. Bar charts of representative PCB signatures from each of the three groups; S-07 from the Canadian group, S-22a from the W. European group 1 and S-19 from the W. European group 2.

4 Discussion

4.1 PCB signatures in different organs

Analysis of individual organs obtained from the same Leach's storm-petrel showed that the PCB signature did not vary greatly between the liver, stomach, guts and heart (Figure 3). This is consistent with previous research which has shown that a similar PCB signature was present in a variety of different tissue samples analysed from the same bird (Boumphrey et al., 1993). The main difference in the signature of organs analysed in this study was observed in the stomach which contained higher proportions of CB-190 and depleted proportions of CB-153. As the contents of the stomach were not completely removed prior to extraction, this difference could be associated with the PCB signature of undigested food within the stomach.

299 Although the PCB signature remained relatively constant between different organs the total
300 concentrations of the EC7 PCBs were more variable. The highest concentration was
301 recorded in the liver (580 μg g^{-1}), which was higher than concentrations recorded in the
302 stomach (150 μg g^{-1}), guts (240 μg g^{-1}) and heart (210 μg g^{-1}). The relative similarity of the
303 PCB signature in different organs (Figure 3) demonstrates that comparisons between birds
304 can be made irrespective of the tissue type sampled. Nonetheless it is preferable to use the
305 same tissue type if direct comparison of PCB concentrations between samples is required.
306 In this study the highest total PCB concentrations were obtained from the liver, which
307 suggests that it is a good tissue type for future studies. Using the liver should provide a
308 higher number of PCBs to be detected compared to other tissue types, leading to a more
309 informative PCB signature.

310 **4.2 Distinguishing differences among individual Leach's storm petrels**

311 Previous attempts to distinguish differences among the 25 wrecked Leach's storm petrels
312 have involved the analysis of stable isotopes and HBIs. While stable isotopes showed no
313 clear differentiation in feather signatures (Bicknell, 2011), interpretation of HBIs provided a
314 division of the samples obtained from Canada and the UK (Brown et al., 2013). In the current
315 study, the application of principal component analysis to PCB data obtained by GCxGC-
316 ToFMS provided additional information. Firstly, principal component analysis of PCB
317 signatures not only distinguished between birds that were collected from Canada and the UK
318 but also identified a further sub-division in the European birds (Figure 4). The HBI analysis
319 showed that the total concentrations and relative distributions of HBI isomers were similar for
320 all Leach's storm petrels recovered from the UK. HBIs provide dietary insights for relatively
321 short periods of time (e.g. <1 month (Brown and Belt, 2012)) and so this relative similarity
322 was interpreted as being consistent with dietary contributions in the weeks prior to the birds
323 being wrecked in December (Brown et al., 2013). This period coincides with the breeding /
324 fledging period (between late May and November) and indicates that during this period the
325 birds were all feeding in a similar area. In contrast to HBIs, PCBs are known to be highly

326 persistent in animals and so the signature is representative of many years exposure
327 throughout the animal's lifetime (Jaspers et al., 2013). The main exposure pathway for
328 animals is usually linked to their diet; therefore variations in feeding patterns could explain
329 the differences in the PCB signatures observed in Figure 4.

330 The diet of the Leach's storm petrel predominantly comprises small fish and zooplankton,
331 although feeding preference has been shown to vary slightly throughout the fledging period
332 and is based on the availability of different food sources throughout the year (Hedd et al.,
333 2009). In Newfoundland fish were identified as the preferential food source and comprised
334 60 - 90% of a storm petrel's diet. Results from Hedd et al. (2009) showed that mature
335 lanternfish (myctophids) which vertically migrate from the mesopelagic during the night were
336 the most consumed food source (78% of identified fish). The higher concentrations of PCBs
337 and higher proportions of the more chlorinated congeners are both indicators that the
338 Western European group 1 birds were feeding on prey from higher tropic levels (Bentzen et
339 al., 2008; Muir et al., 1995), and/or prey from the mesopelagic and deep sea rather than
340 surface water species (Roscales et al., 2011). Analysis of stable isotopes in the blood of
341 breeding Leach's storm petrels revealed regional differences in $\delta^{13}C$ and $\delta^{15}N$, attributed to
342 potential differences in food-web structure/length in each region (Bicknell et al., 2013). The
343 principal component analysis of the PCB signatures supports this hypothesis by indicating
344 the three groups of birds are representative of sub-populations consuming prey from
345 different trophic levels and/or from different regional ecosystems.

346 Biometric variability may also influence the PCB signature of birds. Whilst this study was
347 able to demonstrate that there was no gender based variation, any age related variation
348 could not be investigated because the age of the birds was not known. PCB signatures in
349 long-lived animals, such as humans, have been shown to vary over time due to variable
350 exposure and the subsequent biotransformation and elimination of less persistent congeners
351 (Megson et al., 2013b; Quinn and Wania, 2012). As a result, older individuals tend to have
352 higher total PCB concentrations which are dominated by the more chlorinated congeners.

Whilst this could indicate that the observed sub-grouping of the European birds was a function of age, the absence of a similar division in the Canadian birds, which might also be expected to contain age variation, suggests that this is unlikely.

4.3 Evidence for ocean-wide movement of Leach's storm petrels

There was overlap between the two groups of birds recovered from Newfoundland and the UK. Although S-17 was collected in Newfoundland, PCA revealed it had a PCB signature representative of European birds. In addition to the PCA assignment, this sample also contained higher total PCB concentrations than the other Canadian birds, which was more representative of European birds. This suggests that S-17 was originally from Europe but had migrated across the Atlantic.

There were also four birds (S-23, S-24, S-26 and S-33) collected in the UK that have a similar PCB signature to the Canadian birds. This would suggest these birds originated from the Newfoundland region of Canada. However, as the HBI data for these four birds is consistent with the other birds recovered from the UK it also suggests they were feeding around Western Europe in the weeks leading up to the storm. It is therefore likely that these birds had already migrated to Europe more than a month prior to the storm that subsequently killed them.

These findings provide further evidence of regular movement of individual Leach's storm petrels across the North Atlantic, and the high level of connectivity between regions and colonies as indicated by previous stable isotope and genetic studies (Bicknell et al., 2012; Bicknell et al., 2013).

5 Conclusions

Analysis of tissue obtained from 25 wrecked storm petrels by GCxGC-ToFMS was used to produce a comprehensive data set with 83 specific PCB congeners present in >60% of samples. Analysis of different organs from the same bird showed that the PCB signature did

not vary greatly in samples obtained from the gut, heart, liver and stomach. The data set was interrogated by multivariate statistical analysis which identified different PCB signatures in birds recovered from Canada and the UK. The differences in PCB signatures are believed to be representative of sub-populations consuming prey taxa from different trophic levels and/or utilising different feeding locations although possible influences due to age could not be discounted. There was some overlap in the PCB signatures of birds recovered from Canada and the UK, thereby providing further evidence of regular movement of individual Leach's storm petrels across the North Atlantic and a high level of connectivity between regions and colonies.

The results of this study show how PCB fingerprinting can be a useful tool to study the provenance, geographical movement, and feeding habits of animals such as the Leach's storm petrel. As with any fingerprinting exercise, the most reliable conclusions are drawn from multiple lines of evidence. Previous investigations have shown how HBI and stable isotope analysis of blood and feathers can be used to assess recent movement of individuals. In this study PCBs have been used to identify differences over longer time scales.

The findings highlight the ability of GCxGC-ToFMS to provide the high quality congener specific analysis that is necessary when comparing PCB signatures. This work builds on previous studies using PCB signatures in birds by successfully applying the technique to an understudied pelagic species utilising a large territory and foraging area.

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