



Changes to polychlorinated biphenyl (PCB) signatures and enantiomer fractions across different tissue types in Guillemots

David Megson^{a,b,*}, Thomas A. Brown^{b,c}, Gwen O'Sullivan^d, Matthew Robson^e, Xavier Ortiz^e, Paul J. Worsfold^b, Sean Comber^b, Maeve C. Lohan^b, Eric J. Reiner^e

^a School of Science and the Environment, Manchester Metropolitan University, Manchester M1 5GD, UK

^b Biogeochemistry Research Centre, SoGEES, Plymouth University, Plymouth, Devon PL4 8AA, UK

^c Marine Ecology and Chemistry, Scottish Association for Marine Science, Oban PA37 1QA, UK

^d Department of Earth & Environmental Science, Mount Royal University, 4825 Mount Royal Gate SW, Calgary, Alberta T3E 6K6, Canada

^e Ontario Ministry of the Environment and Climate Change, 125 Resources Road, Toronto, Ontario M9P 3V6, Canada

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ABSTRACT

Two Guillemot carcasses were dissected, each providing 12 discrete tissue samples and 3 samples of partially digested food. One hundred and five PCBs from the 209 PCBs determined by GCxGC-ToFMS were detected. The relative proportions of individual PCBs did not vary greatly within tissue types, although the PCB profile from undigested food could be distinguished. Enantiomer fractions (EFs) were determined for CB-95, CB-136 and CB-149 by GC-HRqToFMS. EFs in the partially digested food were near racemic, with high levels of enrichment for E1 CB-95 in the kidneys and liver (EF of 0.80 and 0.84 respectively). This provides some of the clearest evidence to date that fractionation takes place in the organs where metabolic biotransformation and elimination of PCBs occurs. Our findings also confirm the ability of non-lethal sampling techniques, such as collection of small (< 1 g) blood samples, to provide PCB signatures that are representative of an individual organism.

1. Introduction

Polychlorinated biphenyls (PCBs) predominantly enter animals through ingestion of contaminated food. This can result in the accumulation of PCBs, with higher PCB concentrations usually associated with lipid rich tissues (Maervoet et al., 2005; Karjalainen et al., 2006). Biomagnification can lead to elevated PCB concentrations in top predators (Hansen, 1999; Muir et al., 1988). In most cases the PCB signature in animals can be largely explained by their food source (Jaspers et al., 2013), although human induced changes in land use can also influence the signature (Ferne et al., 2008). Once incorporated, biotransformation and elimination of PCBs can vary from species to species. For example, animals such as bears and humans have been shown to be capable of metabolising some PCBs, while the equivalent capacity has not been observed in predatory birds (Jaspers et al., 2013).

Some studies have provided evidence that the relative proportions of PCBs varies between different tissue types as a result of the preferential accumulation of, for example, ortho-chlorinated PCBs in the brain of rats (Kodavanti et al., 1998). PCBs are highly soluble in lipids and therefore accumulate in tissues and organs according to their respective Kow-dependent release rates (Karjalainen et al., 2006). The

accumulation of PCBs from digested food occurs as PCBs partition across the membrane lining the gastrointestinal tract into the bloodstream. The blood flow in different tissues initially drives the distribution of PCBs until an equilibrium is reached which is primarily driven by the tissue lipid content (Karjalainen et al., 2006). However, despite the variable relative accumulation rates of PCBs, highly similar PCB distributions have been previously measured in birds (Boumphrey et al., 1993), specifically in the gut, heart, liver and stomach tissues from a Leach's storm petrel (Megson et al., 2014). Relatively little is known about the relative proportions of individual PCBs within an organism as a function of the observed non-uniform accumulation, indicating the necessity for further work.

There are 19 out of 209 PCBs that are predicted to exist as stable atropisomers (Oki, 1983). In commercial mixtures both enantiomers are produced in equal proportions and thus are racemic. In animals, metabolic processes such as enzyme mediated oxidation have been proven to preferentially target one stereoisomer, resulting in atropisomeric enrichment (Harrad et al., 2006; Wong et al., 2002; Wu et al., 2014). The degree of enrichment is species specific and can vary for the different enantiomers measured. There is currently little information on how the enantiomer fractions vary in different organs in animals. Chu

* Corresponding author at: School of Science and the Environment, Manchester Metropolitan University, Manchester M1 5GD, UK.
E-mail address: d.megson@mmu.ac.uk (D. Megson).

et al. (2003) showed that PCBs 95, 132 and 149 are near racemic in human muscle, brain and kidney tissue, whereas Kania-Korwel et al. (2010) identified enrichment of CB-95 in the blood, adipose tissue, brain and kidneys of mice.

Here we present the results for the determination of all 209 PCB congeners and three atropisomers in 30 tissue samples obtained from two common guillemot (*Uria aalge*) birds. This study examines potential changes to the PCB signature and enantiomer fraction that may occur in different organs. The results are discussed in the context of providing evidence for the adoption of ethical, non-fatal sampling techniques, such as blood collection, to provide a reliable indicator of the PCB signature in future studies.

2. Materials and methods

For this study we use the common guillemot (*Uria aalge*) to investigate if the relative proportions of PCBs and enantiomer fractions change within an individual organism. The common guillemot is the most abundant seabird breeding in the UK, with an estimated 1 million breeding pairs (Harris and Wanless, 2004). Guillemots are colonial, cliff-nesting seabirds that spend a large proportion of their time at sea foraging for food. The guillemot's diet is primarily comprised of benthic fish from the *Ammodytidae*, *Gadidae* and *Clupeidae* families but also includes a wide variety of invertebrates such as crustaceans, annelids and molluscs (Anderson et al., 2014; Bradstreet and Brown, 1985). The guillemot's diet is known to vary considerably due to the availability of prey.

2.1. Sample collection and preparation

Two guillemot carcasses were collected from the south coast of the UK. The carcasses were in good condition, with minimal degradation or damage, which enabled detailed dissections yielding samples from 12 different tissue types including: the kidney, heart, breast muscle, intestines, leg muscle, liver, blood, brain, pancreas, proventriculus, duodenum and gonads from each bird. Three samples were also obtained from partially digested food from within the gastrointestinal tract including the proventriculus contents, duodenum contents and intestine contents.

PCB signatures were determined by comprehensive two-dimensional gas chromatography coupled with time of flight mass spectrometry (GCxGC-ToFMS) and interpreted using principal component analysis to compare the relative proportions of 74 common PCB congeners in the different tissue types. Enantiomer fractions were determined using gas chromatography coupled with high resolution time of flight mass spectrometry.

2.2. Extraction procedure

Sample extraction was undertaken following the established method for PCB extraction in tissues reported by Megson et al. (2013) and outlined in Brown et al. (2013). All samples were freeze-dried (-45°C ; 0.2 mbar; 72 h) and ground into a powder. Samples were saponified in a methanolic potassium hydroxide solution ($\sim 4\text{ mL H}_2\text{O}:\text{MeOH}$, 1:9; 20% KOH) for 60 min (80°C). Hexane ($3 \times 4\text{ mL}$) was added to the saponified solutions, which were then vortexed (1 min) and centrifuged (1 min; 2000 rpm). Supernatant solutions containing non-saponifiable lipids (NSLs) were transferred to clean vials with glass pipettes and dried using nitrogen to remove traces of $\text{H}_2\text{O}/\text{MeOH}$. NSLs were then re-suspended in hexane (0.5 mL) and fractionated (5 mL hexane) using column chromatography (SiO_2 ; 0.5 g). Samples were evaporated to incipient dryness and reconstituted with $10\text{ }\mu\text{L}$ of an internal standard comprising $^{13}\text{C}_{12}$ PCBs 60, 127 and 159 at a concentration of 10 ng mL^{-1} (CIL-EC-5370 EN-1948-4 PCB sampling standard, LGC) and $90\text{ }\mu\text{L}$ of hexane prior to analysis.

2.3. PCB signature analysis (GCxGC-ToFMS)

2.3.1. Analytical procedure

Samples were analysed to determine the presence of all 209 PCBs using the methods described by Megson et al. (2013) 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 ($60\text{ m} \times 0.18\text{ mm} \times 0.18\text{ }\mu\text{m}$) ^1D column and a Rxi-17 ($1.5\text{ m} \times 0.1\text{ mm} \times 0.1\text{ }\mu\text{m}$) ^2D column. A sample volume of $1\text{ }\mu\text{L}$ 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 $> 10:1$.

2.3.2. Data quality

Analytical blanks were run with each batch of approximately 10 samples. All samples were spiked with a $^{13}\text{C}_{12}$ 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 $\mu\text{g g}^{-1}$. As samples were originally extracted for the analysis of other lipids, PCB recovery could not be accurately determined for each sample; therefore reported concentrations were not corrected based on sample recovery or lipid content. PCBs are located within the lipid fraction, which was quantitatively extracted, therefore any bias should not be significant. Furthermore, because results for enantiomer fractions are relative these values are not biased and recovery correction is not necessary. Limits of detection (LOD) for individual PCBs were in the range $0.1\text{--}5\text{ ng g}^{-1}$ (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 sum of the EC7 congeners for the three samples was $105 \pm 0.9\%$ ($1\text{ }\sigma$).

2.4. Chiral analysis (GC-HRqToFMS)

2.4.1. Analytical procedure

The Enantiomeric Fractions (EFs) of CBs 95, 136 and 149 were analysed based on the gas chromatography conditions specified by Robson and Harrad (2004). Samples were analysed using an Agilent 7890 Gas Chromatograph coupled to a Waters Xevo G2-XS qTOF based on the conditions specified in Megson et al. (2016). The corona voltage was set at 5 mA , the cone gas at a flow rate of 175 L h^{-1} , and the desolvation gas flow set at 175 L h^{-1} . Ionization was undertaken using an atmospheric pressure chemical ionization source at 150°C with the detector run in full scan mode using two target enhanced functions on masses 326 and 360. The two most abundant isotopes of each enantiomer were recorded with a mass accuracy of $< 1\text{ ppm}$.

2.4.2. Data quality

The chromatographic performance of the method was assessed prior to each run of 10 samples by analysing a 1:1:1 mixture of Aroclors 1248, 1252 and 1260. Enantiomeric fractions were calculated as per Harner et al. (2000), whereby $\text{EF} = \text{E1} / (\text{E1} + \text{E2})$, E1 is the first eluting or the (+) enantiomer and E2 is the second eluting enantiomer. Samples where only accepted for quantitation if; the enantiomeric fractions of the three atropisomers studied were $0.50 (\pm 0.01)$ in the Aroclor mixture; the least abundant enantiomer of the pair had a signal to noise (S:N) ratio $> 10:1$; and the isotope ratios were within 20% of their theoretical values. The instrumental LODs were calculated by analysing a standard mixture of CB-95 and CB-149; LODs were established at a concentration of $0.1\text{ pg }\mu\text{L}^{-1}$ per enantiomer. Procedural blanks were prepared for each batch of 10 samples; no chiral PCBs were detected in the blanks above the LODs.

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