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Accumulation and toxicity assessment of polychlorinated biphenyls in black-footed albatross (*Diomedea nigripes*) from Midway Atoll, North Pacific Ocean

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ABSTRACT

Polychlorinated biphenyls (PCBs) are ubiquitous chemicals that were used as additives in capacitors and transformers; and heavy contamination in the past of Midway Atoll, a national wildlife refuge, puts the wildlife, including the black-footed albatross (BFAL), at risk. In this study, we assess the profiles and toxicity of the individual PCB congeners at a natural equilibrium state in various tissues of 1-month old and 4–5-month old BFAL chicks and black-footed and Laysan albatross eggs found on the atoll. In the 1-month old chicks from Midway Atoll, the major seven congeners PCBs 99, 118, 138, 153, 170, 180 and 183 accounted for 36–78% of the total PCBs in the various body parts, and the total PCB concentrations in the bird samples are inversely related to the total body weights. In the 4–5-month old chicks, these same congeners accounted for much lower percentages (7–26%) than in the 1-month-old chicks, with higher amounts of the less chlorinated congeners. The total toxic equivalents (TEQs) for all of the tissues in the 1-month old chicks ranged from 130 to 11,000 pg g^{-1} (lipid weight, lw), and the total TEQs for the 4–5-month old chicks ranged from 18,000 to 100,000 pg g^{-1}. The average total concentration was 7.9 and 4.6 μg g^{-1} lw in the BFAL eggs and Laysan albatross eggs, respectively. The high concentrations could be accounted for by the age and PCB accumulation of the female producing the egg. The average TEQs were 70 and 90 pg g^{-1} in the Laysan albatross eggs and BFAL eggs, respectively. This PCB concentration and toxicity information can be used to determine the toxicological risk of the BFAL chicks while nesting at Midway Atoll, and the analysis of the albatross eggs is an indication of the contamination of the female albatross at the time of egg formation, with the levels acting as an indicator of the total PCB body burdens that the females are experiencing. The information from this study is indicative of the toxicological risk to the seabirds that nest and feed near Midway and of the overall PCB contamination in the North Pacific Ocean.

1. Introduction

Polychlorinated biphenyls (PCBs) are ubiquitously present throughout the world and among the various food chains. PCBs were chemically produced as mixtures and were most commonly used as additives in dielectric fluids in capacitors and transformers (Erickson, 1997). The distribution of PCB congeners differs among the different trophic levels due to environmental degradation, which is dependent on differing solubilities, volatilities, and degradation and/or metabolism of the individual congeners; therefore, the PCB congener distributions in an organism differ greatly from those of the original technical mixtures (Van den Berg et al., 1998). The colonial fish-eating waterbirds of the Great Lakes have been exposed to many toxic organochlorines including PCBs, and the birds and their chicks have been adversely affected with, for example, decreases in reproductive potential (causing population decrease), embryo lethality, and deformities (Giesy et al., 1994; Levengood and Schaeffer, 2010).

Midway Atoll is located in the North Pacific Ocean, approximately 1100 miles northwest of Oahu, Hawaii (approximately 178°W longitude, 28°N latitude) and is made up of two main islands (Sand Island and East Island) that are surrounded by a coral reef. Midway Atoll played a historical role in World War II and was used and modified very heavily by the military during the war and afterwards. Midway Atoll is now part of the Hawaiian Islands National Wildlife Refuge and since May 1996 has been under the control of the U.S. Fish and Wildlife Control. Midway Atoll and the

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waters surrounding it are home to a variety of seabirds, including the black-footed albatross (BFAL) (*Diomedea nigripes*). In the early 1900s, various albatross populations in the tropical North Pacific Ocean decreased due to hunting, but the BFAL population is steadily increasing although the BFAL is still considered a threatened species (Jones et al., 1996; Kubota et al., 2010).

BFAL are frequently found in the northeastern Pacific, Asian, and North American coasts where PCB concentrations are still quite high (Jones et al., 1996). The diet of BFAL is composed of approximately 50% flying fish and flying fish eggs and 32% squid (Auman et al., 1997; Finkelstein et al., 2006). BFAL have larger body sizes than other albatross species and may have a higher feeding rate to maintain their body size, so the feeding habits and body size of BFAL influences its organochlorine accumulation (Guruge et al., 2001a,b). The albatross is at the top of the food chain; therefore, the PCB levels of BFAL are an indicator of the exposure and toxicological risk for other seabirds feeding in the North Pacific and nesting near Midway Atoll.

The objectives of this study were to (1) determine the contamination levels, compositions and distribution of PCBs in the tissues of BFAL chicks from Midway Atoll as well as in eggs laid on the atoll, (2) determine the toxic equivalents (TEQs) in bone, head and neck, liver, muscle, internal organs, and skin tissue samples of BFAL chicks and BFAL and Laysan albatross eggs from Midway Atoll, and (3) compare the PCB levels and compositions to other similar studies.

2. Materials and methods

2.1. Sample information

The samples were collected in January to June of 2001. Three chick carcasses of B8-32, Bulky Dump (BD)-77, and BD-88 were approximately 1 month old. Three older chick (OC) carcasses were collected from the BD sites and were approximately 4–5 months old, just about ready to fledge. The carcasses were wrapped in teflon-lined aluminum foil and stored until transfer to the laboratory. Seven unhatched and/or abandoned eggs were collected from sites B8 and BD. The contents of the egg were placed into a clean jar and stored until transport to the laboratory. All samples were stored at −20 °C until preparation for analysis.

In the laboratory, after the feathers were removed and the total mass was weighed, the bird was then dissected into bone, head and neck, liver, muscle, organs (other than liver) and skin. The different tissues were homogenized separately with dry ice and lyophilized. The albatross eggs were homogenized with dry ice and lyophilized. The dried materials were placed in an airtight container until supercritical fluid extraction (SFE).

2.2. Extraction and cleanup

The lyophilized tissues and eggs were extracted with an Isco SFX 220 extractor (Isco, Inc.; Lincoln, Nebraska) following the procedure of Miao et al. (2000, 2001) with slight modifications. These lyophilized tissues and egg samples (~1.0 g) were placed into the 10 ml extraction cells, and 3 g of acidic alumina (60–325 mesh) was placed at the bottom of the cell to retain lipids during SFE. A static extraction process was performed at 6000 psi pressure and a temperature of 150 °C for 10 min and followed by a dynamic extraction at the same pressure and temperature with 80 ml of supercritical CO_2 at a flow rate of 2 ml min^{-1}. A gravimetric determination was made for the amount of extracted lipids. The extracts were dissolved with *n*-hexane and washed with concentrated H_2SO_4, followed by column chromatography (column consisted of 3% deactivated silica, 6% deactivated alumina, and 1 cm of anhydrous sodium sulfate). The column was eluted with 20 ml of dichloromethane/hexane (1:2, v/v) to yield the PCBs fraction. The extract was dried with anhydrous Na_2SO_4 and concentrated to 20 μl under a gentle high purity nitrogen stream for gas chromatograph/electron capture detection/ion trap MS (GC/ECD/ITMS) analysis. Each sample was analyzed in triplicate.

2.3. Gas chromatograph/electron capture detection/ion trap ms (GC/ECD/ITMS) analysis

The samples were analyzed on a Varian Saturn 2000 (Palo Alto, CA) gas chromatograph with simultaneous mass spectrometric (ion trap) and electron capture detection (GC/MS and GC/ECD, respectively). The column flow was split between the ECD and the MS in a 1:10 ratio, respectively. The column was a capillary column ZB-1 (60 m × 0.25 mm *i.d.* × 0.25 μm film) (Phenomenex, Torrance, CA) with helium as the carrier gas and nitrogen as the makeup gas for the ECD. The oven temperature was linearly ramped from 120 °C at 2 °C min^{-1} to 275 °C (hold 10 min). The injector and ECD detector were set at 280 °C and 330 °C, respectively. The temperature of the ion trap was 200 °C, the manifold 80 °C, and the transfer line 210 °C. The individual PCB congeners were identified with retention time correlation to PCB standards (Accustandard Inc., New Haven, CT) and mass spectral matches. Concentrations of each PCB congener were calculated from external PCB standards with ECD data and confirmed with the MS. PCB concentrations for the BFAL tissues were calculated on a dry weight and lipid weight basis. The PCB concentrations for the eggs were calculated on a lipid weight basis.

2.4. Quality assurance and quality control (QA/QC)

Average PCB recoveries and relative standard deviation (RSDs) were first obtained to evaluate the method performance by multiple analyses of ten tissue samples spiked with PCB standard C-CS-08 (Accustandard, New Haven, CT), which contained PCBs 30, 43, 55, 58, 76, 109, 112, 120, 159, 186, 192, and 198) (Supporting Information Table S1). The spike level of each PCB was approximately 50 ng g^{-1}. A solvent blank and matrix blank were analyzed through the entire procedure prior to and after every 10 samples. Standard solutions of PCBs were run at the beginning of sample analysis to determine the relative response factors and evaluate peak resolution. Each sample was analyzed in triplicate unless otherwise stated.

The limits of detection (LOD) were determined as signals 3 times the background signal. Peaks that were smaller than 3 times the signal-to-noise ratio were not considered. The LOD for PCBs ranged from 1 to 50 pg g^{-1}, were dependent upon the degree of chlorination of the different congeners, and were approximately 5 pg g^{-1} for most congeners. Reported PCB concentrations were not corrected according to the recoveries.

3. Results and discussion

3.1. PCB concentrations in 1-month old chicks and toxicity assessment

Table 1 shows the concentrations of total PCBs in every body tissue of the 1-month old BFAL chicks. The total PCB concentrations in the three birds are inversely related to the total body weights. B8-32 is the smallest 1-month old chick, weighing only 146 g, and contained the highest total PCB concentration (191 μg g^{-1} lw). BD-88 (309 g) and BD-77 (413 g) contained 118 μg g^{-1} lw and 37 μg g^{-1} lw of total PCBs, respectively. The total PCB body burdens of B8-32, BD-88 and BD-77 are 3.7, 2.7 and 1.8 mg g^{-1} (dry weight, dw) and 4.0, 5.3 and 2.2 mg (lw), respectively.