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Polychlorinated Biphenyls in Eggs of Spectacled Eiders (*Somateria fischeri*) from the Yukon-Kuskokwim Delta, Alaska

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Organochlorines (OCs) such as polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) and its metabolites have deleterious effects on fish and wildlife (Blus 1996; Peakall 1996; Hoffman et al. 1996; Wiemeyer 1996). OCs have been found in tissues of Arctic and sub-Arctic animals (Galster and Burns 1981; Barrett et al. 1996; Blais et al. 1998; Kucklick et al. 2002). Bioaccumulation of OCs in remote polar regions indicates that OCs undergo a long-range transport (Gouin et al. 2004).

The United States Fish and Wildlife Service listed spectacled eiders as a threatened species in 1993 (U.S. Fish and Wildlife Service 1993) under the U.S. Endangered Species Act after documentation of severe declines in numbers of breeding pairs on the Yukon-Kuskokwim Delta, Alaska (Stehn et al. 1993). One potential cause for the eider population decline is that the marine environment changes have led to increased contaminant loads (Trust et al. 2000).

Levels of PCBs in birds have frequently been linked to eggshell thinning and reduced reproductive success and bird population declines (Cooke et al. 1976; Clark et al. 2001; Mañosa et al. 2003; Gilbertson et al. 1991; Walker et al. 2001). Background data of PCBs in spectacled eiders from Alaska may be helpful to understand the causes for eider population decline, but to the best knowledge of ours, there have been little information on PCBs concentration and congener distribution in spectacled eiders in this area. The objective of this work was to obtain baseline data of PCBs in spectacled eider eggs collected from the Yukon-Kuskokwim Delta, Alaska.

MATERIALS AND METHODS

Thirteen spectacled eider eggs were collected after being identified as infertile or salvaged from abandoned nests from the Yukon-Kuskokwim Delta, Alaska, in June to July 1995. The eggs sampled were stored at -10 °C during 1995-2001, and shipped on dry ice to the analytical laboratory (Honolulu, HI) in Feb, 2004, where the samples were stored at –25 °C until the analysis. Prior to the sample process, egg weight, maximum breadth and length were measured, and then each egg was washed with deionized water, disinfected along the equator with 70% ethanol in water, and rinsed with deionized water again. The eggshell was cut

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Table 1. Egg size, weight, eggshell thickness, and lipid contents.

Egg ID	Length (mm)	Breadth (mm)	ww (g)	dw (g)	Shell (mm)	Lipid (%)[a]	∑PCBs (ng/g ww)
DVP017-2[b]	66.8	44.0	44.6	15.4	0.364	18.5	36.1
DVP065-1	66.8	41.4	53.4	18.7	0.330	15.6	24.8
DVP065-2	65.5	42.6	50.0	16.5	0.356	16.1	44.9
DVP065-3	69.9	41.9	48.6	16.5	0.347	16.3	25.1
DVP065-4	68.7	45.7	54.8	18.8	0.305	21.0	16.7
DVP065-5[c]	68.2	44.3	54.6	25.3	0.339	12.2	38.1
DVP058-3[b]	66.8	45.5	59.9	15.1	0.279	11.0	14.2
DVP058-4[b]	63.8	43.2	55.7	15.2	0.347	16.1	14.3
PLF063-2[d]	65.1	45.8	57.2	18.9	0.364	15.0	34.7
PLF028-3[e]	69.7	43.4	56.2	19.4	0.373	13.3	17.5
PLF066-1[f]	67.1	44.2	58.0	17.6	0.296	14.1	23.3
PLF066-4	72.6	39.8	61.9	19.0	0.339	14.0	14.9
PTK135-5[f]	70.6	44.9	65.6	21.3	0.398	18.5	6.60

[a] lipid was calculated on wet weight.
[b] nest abandoned during laying after partial predation
[c] nest contained 5 eggs all of which were infertile.
[d] one egg out of a clutch of 4 was infertile.
[e] nest abandoned following predation during incubation.
[f] two eggs of a clutch of 6 were infertile.

along the equator, and the contents were transferred to a pre-cleaned glass container. Two eggs (DVP 058-3 and DVP 058-4) were found containing embryo (Table 1). A half of a shell was air-dried, and the shell thickness was measured with a calibrated micrometer.

The egg yolk and white were homogenized, lyophilized and extracted by using two different accelerated solvent extraction (ASE 200, Dionex, Salt Lake City, USA) procedures. The first procedure: 6-7 g of the dried egg contents and 12 g of silica gel (activated at 450 °C overnight) were ground until the free flowing mixture obtained, in which silica was used to retard part of lipids (Gomez-Ariza et al. 2002). The mixture was transferred to two 22-mL extraction cells, and extracted at 60 °C and 2000 psi with a mixture of methylene chloride and hexane (15:85, v/v). After two 10-min static extractions, fresh solvent was introduced to flush the lines and cell. The flush volume amounted to 1.5 fold of the extraction cell volume (1.5×22 mL). This extract was used for PCB analysis. The second procedure: 0.2-0.7 g of dry egg content was extracted in 11-mL cells with the same solvent at a higher temperature (125 °C) and a pressure of 2000 psi. The static time and static extraction cycles were 5 min and 3 cycles, respectively. The flush volume was 60% of the extraction cell volume. The extracts were used for the determination of extractable lipid contents by gravimetric after solvent removal under a gentle nitrogen stream and in an oven at 60 °C for overnight.

The extract (55 mL) from the first extraction procedure was concentrated to 2 mL with a rotary evaporator and under a gentle nitrogen stream, and then purified with a glass column packed with 40% sulfuric acid modified silica gel, followed by a glass column packed with 2% water deactivated florisil. PCBs were eluted with 10% methylene chloride in hexane and 45 mL of hexane, subsequently. The hexane fraction was concentrated to 50 μL for the instrumental analysis.

PCBs were analyzed with a Varian 3800 GC/Saturn 2000 ion trap mass spectrometer (Varian, Walnut Creek, USA). PCB congeners were separated on a 60 m ZB-1 column (0.25 mm i.d., 0.25 μm film thicknesses, Phenomenex, Torrance, CA, USA). The carrier gas was helium at a constant flow of 2 mL/min. The GC oven temperature was programmed from 120 °C to 275 °C at 2 °C/min, and held for 10 min at 275 °C. The GC injector, transferring line and ion trap temperatures were 300 °C, 280 °C and 200 °C, respectively. The injection volume was 2 μL. The mass spectrometer was operated in MS/MS mode, and data were analyzed with Saturn GC-MS Workstation v 5.4 software. Optimum excitation amplitudes were at 1.60 v for di- and triCB, 1.80 v for tetraCB, and 2.60 v for penta- to decaCB. The optimal excitation storage levels were 73.2, 112.8, 128.8, 152.8, 168.8, 173.9, 189.8, 204.8, and 219.9 for di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and decaCBs, respectively. Excitations time and isolation time were set at 15 ms and 7 ms, respectively. PCBs were identified with their retention time compared to that of the corresponding authentic standards, signal-to-noise of greater than 3 for the selected ions, and chlorine isotope ratio of at least two characteristic ions matching the theoretical values within 20% deviation. Quantifications of PCBs were performed by using an external standard method. The PCB congener calibration mixtures (C-CS-01 to C-CS-05) were purchased from AccuStandard, Inc (Newhaven, CT, USA) and consisted of 144 PCB congeners.

Average recoveries and relative standard deviations (RSD) of PCBs from the four matrix-spiked chicken egg samples (C-CS-01 at a level of 3.33 ng/g of each PCB congener) ranged from 89% to 126% with RSD of 8-25%, except that recoveries of PCBs 21, 50 and 65 were higher than 130 %. The method detection limits (MDL), evaluated by three times standard deviations, and ranged from 0.0026 to 0.0102 pg/g ww.

RESULTS AND DISCUSSION

Among the 144 PCBs analyzed, only 28 congeners were detected in the eider eggs. The dominant congeners were PCBs 33, 44, 41/64, 118, 128, 138 and 153 (Figure 1). PCBs 153, 138, 118, and 128 were also found to be the predominant congeners in breast muscles and livers of common eiders in Iceland (Olafsdottir et al. 1998) and Alaskan Murre *(Uria* spp.) eggs (Pol et al. 2004). PCBs 118, 138 and 153 covered large ratios in commercial mixtures such as Aroclor 1254 (Schwartz et al. 1993). These PCBs are less lipophilic than higher chlorinated ones (octa-, nano- and decaPCBs), but are more readily bioavailable to organisms

in surrounding environment because they are not as tightly bound to sediments as the higher chlorinated PCBs (McFarland and Clarke 1989). Di-*ortho* PCB congeners with chlorines at *para* and *meta* positions in both rings are non-degradable in invertebrates and vertebrates such as fish (Bright et al. 1995; Kannan et al. 1995) and sea birds (Borlakoglu et al. 1990). For example, PCBs 118, 138 and 153 share the characteristic of having chlorine atoms in positions 2, 4 and 5 in one (PCBs 118 and 138) or both rings (PCB 153). The preferential bioaccumulation of less chlorinated congeners (PCBs 28/31 and 33 of triCBs) were also observed by spectacled eider ducks, which may be due to their greater polarity and water solubility relative to highly chlorinated ones (Hawker and Connell 1988) and slow metabolism of the PCBs by spectacled eider ducks. These results may also indicate that the triCBs are more readily transferred to eggs during gestation than higher chlorinated PCBs.

Although similar PCB profiles were found among the five eggs collected from the nest DVP 065, PCB congener concentrations varied greatly (Figure 1). The egg DVP 065-2 contained higher levels of PCBs than the other four eggs. The possible reasons were that the eggs in the same nest were laid from the different duck hens. In spring, breeding pairs of eider ducks move to wet coastal tundra to build nests near shallow ponds or lakes, where food supplies are available. It implies that eider ducks may be exposed to varying sources of PCBs during a season.

Total PCB concentrations (∑PCBs) ranged from 6.3 to 54.7 ng/g ww (45-350 ng/g lipids) in eider eggs. Concentrations of PCBs less than MDLs were calculated as zero. The international toxic equivalents (I-TEQ) averaged to 0.00024 pg/g ww, which was attributed by only PCB 118. Although contaminant levels in the bird eggs have frequently been linked to eggshell thinning and reduced reproductive success (Anthony et al. 1999; Cooke et al. 1976; Ormerod and Tyler 1992; Gilbertson et al. 1991), no correlation was observed between the PCB concentrations and the eggshell thickness (r^2=0.065, P>0.40) in our study.

Similar concentrations of PCBs in some eider species in a few studies have recently been reported. ∑PCBs was less than 100 ng/g ww in 9 livers of common eider collected in west coast of Spitsbergen, Norway in May 1980 (Norheim and Kjos-Hansen, 1984). Thirty PCB congeners at a cumulative level of 121 ng/g ww were detected in breast muscles of common eider in Sker-Jafjörður, Iceland in February, 1993 (Olafsdottir et al. 1998). Savinovaa et al. (1995) reported ∑PCB (19 congeners) levels from 0.8 to 54.3 ng/g ww in tissues (liver, muscle and brain) of common eider collected in Barents Sea, Norway in July-August 1991. ∑PCB ranged from 10 ng/g ww to 150 ng/g ww in livers of common eider sampled in Svalbard Region, Norway in July 1990 (Mehlum and Daelemansb 1995). In 44 livers and kidneys of common eiders collected in Alaska and arctic Russia during 1991-1995, lower concentrations of PCBs (0.55 ng/g ww) were found (Stout et al. 2002). Although more than one hundred of PCB congeners

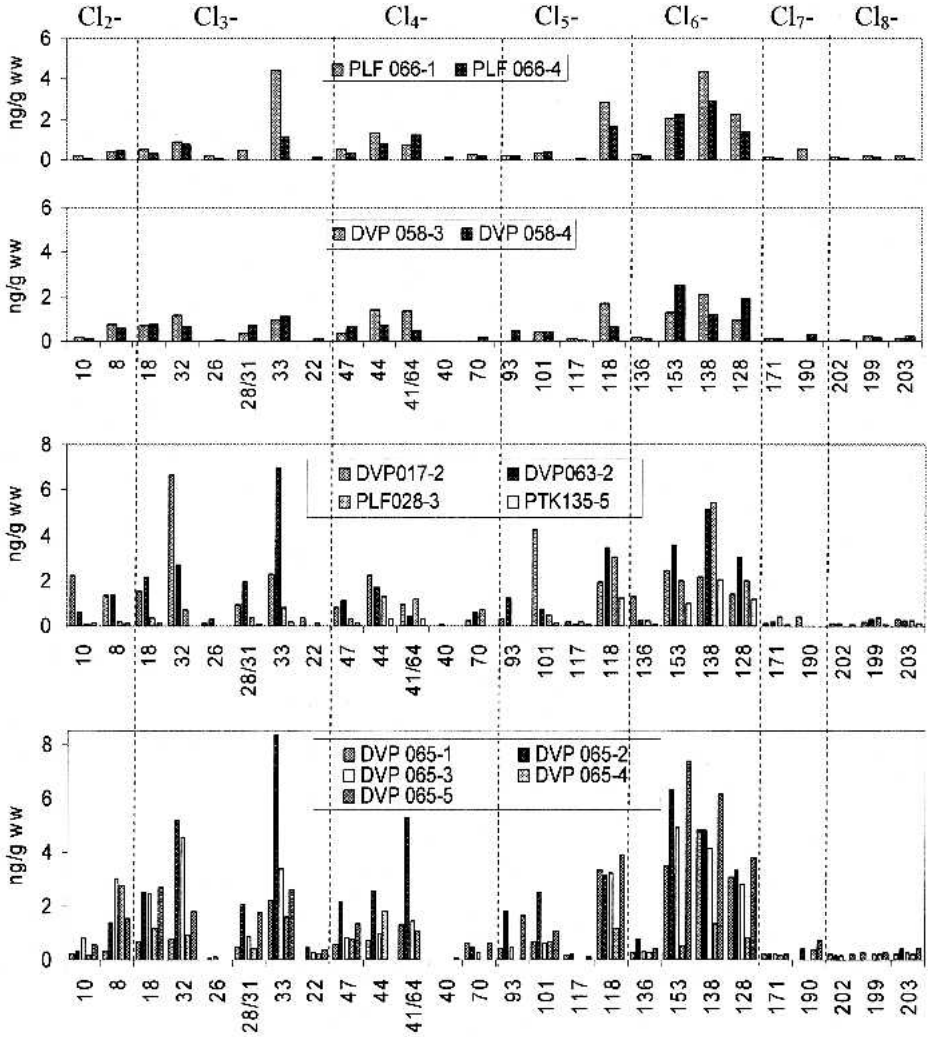

Figure 1. Concentrations (ng/g ww) of PCB congeners in 13 eider eggs from seven different nests.

were detected, ∑PCB ranged from 5 ng/g lipids to 49 ng/g lipids in muscles and livers of eiders from Nuuk, Southwest Greenland in 2000 (Johansen et al. 2004), and averaged 15.12 ng/g ww in 20 eggs from long-tailed ducks and nesting common eiders sampled in Beaufort Sea Alaska in 2000 (Szaro et al. 1979; Franson et al. 2004).

Spectacled eiders feed on bottom-dwelling mollusks, crustaceans, aquatic insects, and vegetation. Feeding habits were possibly related with lower PCB

bioaccumulation in eiders compared with those in the Alaskan fish-eating birds such as murre eggs (Pol et al. 2004). Although ∑PCBs in the spectacled eider eggs were below possible harmful levels (Stout et al. 2002; Trust et al. 2000), the results showed that the eider ducks were exposed to PCBs, and PCBs can transfer from eider hens to eggs.

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