LEVELS AND ISOMER DISTRIBUTIONS OF HEXABROMOCYCLODECANE AND DECHLORANE PLUS IN EGGS FROM CALIFORNIA PEREGRINE FALCONS (*FALCO PEREGRINUS*)

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Introduction

Peregrine falcons in California sit atop both the aquatic (coastal nest sites) and terrestrial (interior or urban nest sites) food webs. We found high levels of polybrominated diphenyl ethers (PBDEs; 0.08-53.1 ppm; median 4.53 ppm) in eggs from California peregrine falcons (n=90 eggs collected 1986-2007 from 52 birds nesting at 38 coastal and interior/urban sites), with levels doubling each decade (r=0.55, p<0.01) [1]. California has the most stringent flammability standard for upholstered furniture (Technical Bulletin 117) and PBDEs have been used extensively to meet this standard. As the use of PBDEs becomes restricted, alternative flame retardant (FR) additives are being introduced into textiles, furniture upholstery, plastics, and electronics. Some of these alternative FRs are now appearing in abiotic and biotic environments [2,3,4].

Two alternative FRs, hexabromocyclododecane (HBCD) and dechlorane plus (DP), are of concern due to their large production volume and long-term use. HBCE levels in San Francisco Bay sea lions increased more than two orders of magnitude between 1993 and 2003 [5]. HBCD (US production/imported volume = 10-50 M lb) is increasingly used as a substitute for PBDEs in thermal insulation building material, upholstery textiles, and high impact polystyrene (HIPS) plastic for electronics [6]. HBCD shares some toxicities with PBDEs, including thyroid disruption and developmental/reproductive abnormalities [7,8,9]. DP (US production/imported volume = 1-10 M lb) is less bioaccumulative and has lower toxicity than HBCD. DP has been widely used in electrical wires and cables, and plastic roofing materials for a long time (> 30 years), and is now ubiquitous in the environment [3], including peregrine falcons [10].

We report levels and isomer distributions of HBCD and DP in eggs (n=40) from peregrine falcons from California.

Materials and Method

We measured levels of two non-PBDE halogenated FRs (HBCD and DP) in peregrine falcon eggs (n=40), i.e. a subset of eggs collected in California over the last two decades (1990-2007) from coastal or interior nests (described in Park et al 2009) [1]. Lyophilized egg samples were extracted using accelerated solvent extraction (Dionex ASE 200) and purified by size exclusion chromatography (Envirosep-ABC, 350 × 21.1 mm column). The extracts were separated into two fractions using a solid-phase extraction (SPE) column (2 g silica gel): eluting with 6.5 mL 60:40 hexane/DCM gave us fraction one, containing HBCD; subsequent eluting with 8 mL DCM gave us fraction two, which contained DP,. Fractions were spiked with internal standards (^{13}C-labelled syn and anti-DP, and d_{18}-labelled α-HBCD). HBCD isomers (alpha, beta, gamma) were analyzed using UPLC (Waters)/MSMS (ABSciex 3200QTrap) with a bridged ethyl hybrid (BEH) C_{18} column (150 mm, 2.1 mm i.d., 1.7 µm particle diameter) in ESI/MRM mode . DPs (anti- and syn-) were analyzed using GC-MS (Agilent 6890) equipped with a 15 m DB-5 HT column (0.25 mm i.d., 0.1 µm, J&W Scientific, Agilent Tech.) in ECNI-SIM mode.

Results and Discussion

HBCDs and DPs were detected in almost all eggs, with eggs from coastal and interior nests showing similar levels. Median levels (ng/g lipid) were two orders of magnitude lower than PBDEs: DPs = 72.7; HBCDs = 84.9; PBDEs = 8493. Levels and Isomer patterns of HBCDs were similar to those found in other studies (Gauthier et al 2007; Covaci et al 2006): alpha (92%) > beta (2%) > gamma (1%), except for the few eggs showing a larger fraction (61%) of gamma HBCD (Figure 1), indicating recent exposure.

DP levels (geomean = 58.3 ng/g lipid) in eggs from California Peregrine Eggs (PFEs) were slightly higher than levels in eggs from Canadian peregrines (geomean = 36.4) [10], as was the anti-/syn-DP ratio (fraction of anti-DP (f_{anti})): California PFE = 0.63 vs. Canadian PFE (0.58), reflecting commercial mixtures (OxyChem = 0.65-0.80) [10]. DP levels in California PFEs were higher than Canadian PFEs close to the manufacturing source of DP (Great Lakes). Eggs from urban California nest sites showed significantly higher levels of DPs (113 ng/g lipid) than eggs from coastal nests (32.8 ng/g lipid) ($p<0.05$), but HBCD levels were not significantly different.

Neither HBCD or DP showed significant temporal trends, while PBDEs continue to increase [1].

This is the first report of non-PBDE FRs in California PFEs. The findings of HBCDs and DPs in eggs from both coastal and interior nests in California indicate that these unregulated/toxic FRs escape from consumer products and bioaccumulate in both aquatic and terrestrial food webs. We continue to monitor levels of these and other non-PBDE flame retardants.

Acknowledgement and Disclaimer

We thank the many ornithologists and bird enthusiasts who have helped the US peregrine populations to survive the DDT-induced egg-shell thinning and reproductive failures of the mid-1950s-60s, and have helped to increase the California breeding population from a low of 2 pairs to >200 over the past thirty years. The views expressed herein are those of the authors and do not necessarily reflect those of Department of Toxic Substances Control, California Environmental Protection Agency.

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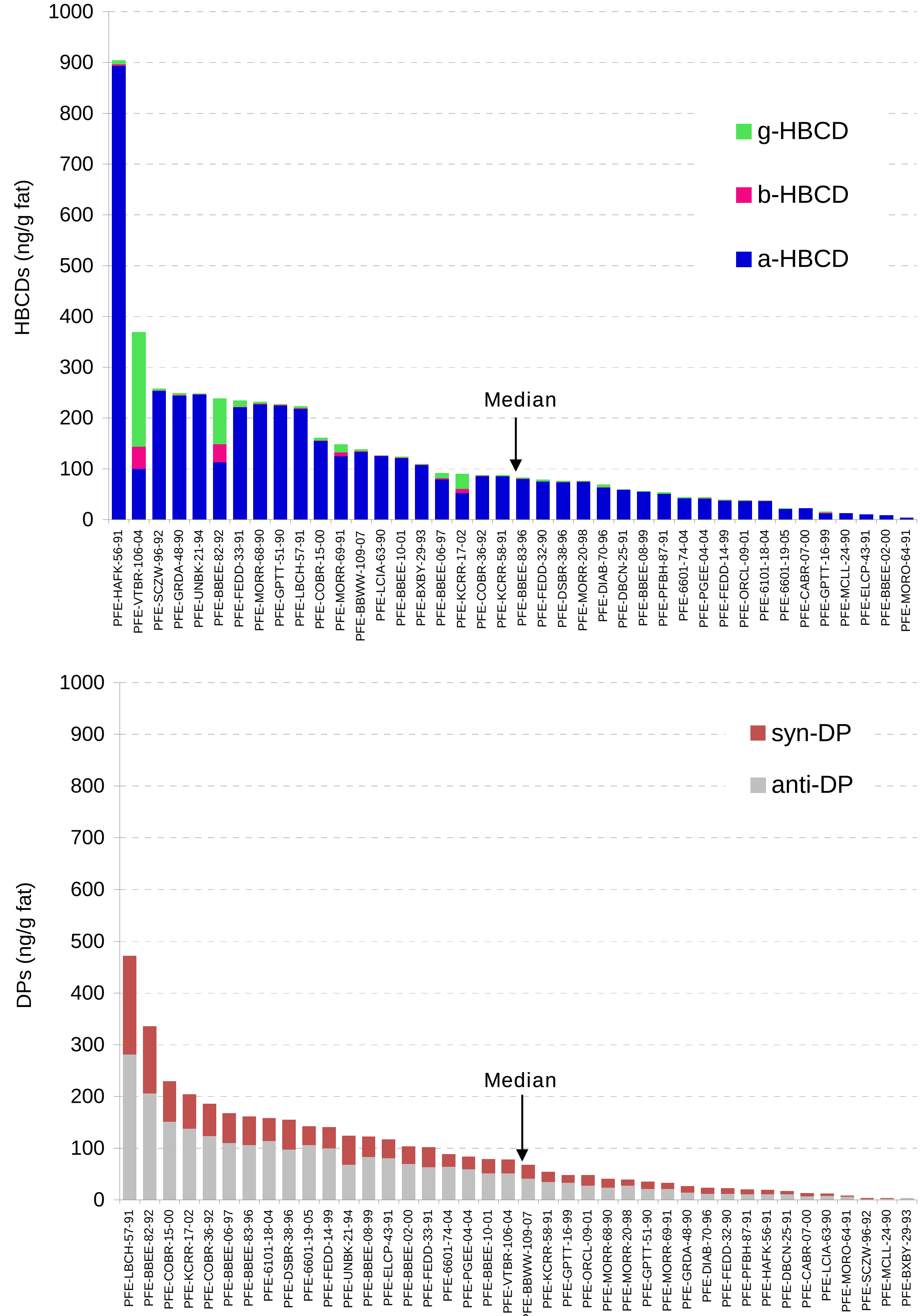

Figure 1. Levels and isomer distribution of hexabromocyclododecane (top) and dechlorane plus (bottom).